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Development of Methods for Sampling and Analysis of Particulate and Gaseous Fluorides from Stationary Sources

Little, Inc.

prepared for

Environmental Protection Agency

NOVEMBER 1972

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FINAL REPORT

DEVELOPMENT OF METHODS FOR SAMPLING AND ANALYSIS OF PARTICULATE AND GASEOUS FLUORIDES FROM STATIONARY SOURCES

prepared for the

ENVIRONMENTAL PROTECTION AGENCY
DURHAM, NORTH CAROLINA 27701
CONTRACT NO. 68-02-0099

ARTHUR D. LITTLE, INC.
CAMBRIDGE, MASS. 02140

NOVEMBER 1972

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A study was conducted which has resulted in the development of tentative sampling and analysis of fluorides emitted from various stationary sources. The study was directed toward developing and understanding the kinds of species which are present in each source emission. This report presents the following information: (1) a review of the various unit processes within the primary aluminum, iron and steel, glass and phosphate processing industries; industry flow diagrams which include estimates of fluoride throughout; and an inventory of emission species found within each process; (2) descriptions of sampling apparatus and procedures for gaseous and particulate fluorides, evaluations of the reactivity of sampling train components and sample container materials in the presence of fluoride ion, and a description of recommended apparatus for each industry; (3) development of analytical methods for measuring fluoride ion; (4) analysis of field samples collected from each industry to identify the chemical species present and to evaluate the suitability of developed analytical methods for measuring fluoride; (5) recommendations for tentative sampling and analysis methods for gaseous and particulate fluoride.

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(Final Report)

April 1972

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Prepared under Contract No. 68-02-0099

for the

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by

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I. SUMMARY

This study, conducted by Arthur D. Little, Inc., for the Environmental Protection Agency, has resulted in the development of tentative sampling and analysis of fluorides emitted from various processes within the primary aluminum, iron and steel, phosphate rock processing and glass manufacturing industries. In most cases, distinction is made between gaseous, insoluble particulate and soluble particulate fluoride species.

Stack emissions from most of the processes that were considered can be sampled in a manner that separates the particulate from the gaseous species. For the tentatively recommended procedure, the particulate is collected by means of a filter or electrostatic precipitator heated above the water dewpoint with gaseous fluorides subsequently collected in a series of water impingers maintained at room temperature. Some very wet process streams, such as for the production of diammonium phosphate (DAP), include considerable water entrainment, precluding a particulate collector. In this case, the particulate is collected in the impingers, and soluble particulate fluoride cannot be distinguished from gaseous fluorides.

Chemical analysis procedures have been developed which emphasize procedural simplicity but which also provide reliable and reproducible results. The fluoride specific ion electrode has been found to be the most suitable approach for measurement of fluoride concentration. Direct measurements on impinger solutions after appropriate buffering appears feasible in many cases. Otherwise, fusion and distillation procedures are required to assure solubilization and separation from interfering species.

The tentative source method for fluorides utilizing the Standardization Advisory Committee (SAC) format is presented in Appendix A. A program providing for field evaluation of these tentative sampling and analysis methods for stationary source fluoride emissions is recommended.

II. INTRODUCTION

In response to growing public demands for clean air, a considerable effort is being expended by the Government in the identification of air pollution sources and the specification of appropriate abatement procedures. Fluoride emissions from several types of industries have been recognized as being harmful to ground vegetation, including "citrus" fruits and gladiolus, as well as cattle and other live stock. The medical effects on human population exposed to fluoride emissions are not well known. The major stationary sources of particulate and gaseous fluoride emissions have been associated with the industries that employ high fluoride-bearing raw materials or use fluorides as a part of their manufacturing process. These industries include steelmaking, primary aluminum, phosphate rock processing, and the manufacture of glass and ceramics.

To arrive at realistic estimates of the fluoride mass emissions burden to the atmosphere and in order to specify appropriate control and abatement methods for fluoride emissions, it is necessary to develop reliable sampling and analysis procedures for gaseous and particulate fluorides which are not encumbered by interferences from other species in the stack gases. The current program is directed toward developing and understanding the kinds of species which are present in each source emission and, in light of these species, to establish tentative methods for representative sampling of these streams and analysis of gaseous and particulate fluoride components. A follow-on study is anticipated in which the recommended procedures will be field tested under the varying conditions that exist within the several unit process operations in each of the four stationary source industries of concern. The experience gathered during field testing would provide an opportunity for making modifications to the sampling and analysis procedures, if deemed appropriate. The collected fluoride emissions data would be available as a resource to EPA in setting design and operating specifications for flue gas pollution control equipment.

The following sections cover:

- A review of the various unit processes within the primary aluminum, iron and steel, glass and phosphate rock processing industries; industry flow diagrams which include estimates of fluoride throughout; and an inventory of emission species encountered within each process.
- Descriptions of sampling apparatus and procedures for gaseous and particulate fluorides, including present industrial practice, evaluations of the reactivity of sampling train components and sample container materials in the presence of fluoride ion, and a description of recommended apparatus for each industry.
- Development of analytical methods for measuring fluoride ion, including procedures for separation and measurement in the presence of interfering species.
- Analysis of field samples collected from each industry to identify the chemical species present and to evaluate the suitablility of developed analytical methods for measuring fluoride.
- Recommendations for tentative sampling and analysis methods for gaseous and particulate fluoride.

III. STATIONARY SOURCE INDUSTRIES

A. General

This study is restricted to consideration of four industries which, because of the raw materials utilized in the chemistry of process relations, are known to emit gaseous and particulate fluorides. These industries are primarily aluminum, iron and steel, phosphate rock processing and glass manufacturing. Some typical fluoride emission control is typically practiced for all unit operations in these industries. The glass industry limits control to collection of particulate dispersoid and fume by baghouse techniques while the other industries rely heavily on wet scrubbers which can be very efficient for the collection of water-soluble gaseous fluorides, including HF, F_2 and SiF_4.

A recently completed comprehensive study of the engineering and cost effectiveness of fluorides emission control for industrial sources was carried out for the EPA by Resources Research, Inc., and TRW Systems Group.(1) The study tasks of their program included an inventory of fluoride emitting processes, process modeling, assessment of the state-of-the-art of measurement and control technology, determination of control costs, projection of trends to the year 2000, and recommendations for research and development programs required for minimizing soluble fluoride emissions in a cost effective manner. Descriptions of the various stationary source industries, including production trends, unit process operations, emissions control methods, and fluoride emission inventories, were presented in detail. Since this extensive background is available, this report will be limited to reviewing the processing operations that contribute most heavily to fluoride emissions.

To supplement data presented in the RRI/TRW report, we have prepared flow diagrams showing materials flow, unit processes and the fate of fluorides (expressed as fluorine) for the major emission sources. These diagrams are presented in Figures 1 and 4. Fluorine emission estimates are based upon the RRI/TRW results as well as data from the Bureau of Mines and our own files; the estimates for fluoride emissions from the scrubbers of the various phosphate rock processing industries are those of RRI/TRW. Within the glass industry, the only major source of fluoride emissions is in some of the special pressed ware products including opal glass, leaded glass and many of the technical-grade products.

B. Industrial Processes

1. Primary Aluminum. A schematic sketch of the unit processes and materials flow of a primary aluminum facility is presented in Figure 1. Aluminum metal is produced exclusively by the electrolytic refining of purified alumina ore that is obtained from the mineral bauxite, a hydrated aluminum oxide having the oxides of iron, silicon and titanium as impurities. Electrolysis is carried out in a carbon black-lined reduction pot which is fitted with carbon electrodes. The bath is a mixture of fused cryolite (Na_3AlF_6), fluorspar (CaF_2), and sodium fluoride (NaF). The primary electrolysis reaction is:

$$2\ Al_2O_3 + 3\ C \rightarrow Al + 3\ CO_2$$

The stoichiometric ratio yields about 20,000 cubic feet of CO_2 per ton of aluminum. Actual gas production is somewhat higher since appreciable quantities of carbon monoxide are also present. The fluoride salts do not take part directly in the reaction, but fluorine compounds, including cryolite and chiolite ($Na_5Al_3F_{14}$), are carried off in the exhaust gases along with the evolution of substantial quantities of CO_2.

The top of the bath is covered with a frozen crust of alumina which dissolves into the cryolite bath as aluminum production proceeds. The carbon electrodes are renewed as they are consumed. There are two types of electrodes in use. One is the prebaked electrode which is periodically lowered into the bath until the stub end is reached. Another is the so-called Soderburg electrode which is charged to the operation as a paste and is baked into a hard electrode by the process heat as it is lowered into the pot. Makeup cryolite and fluorspar are also apread on top of the crust as required along with the alumina charge. The molten aluminum sinks to the bottom of the bath and is withdrawn through a tap-hole.

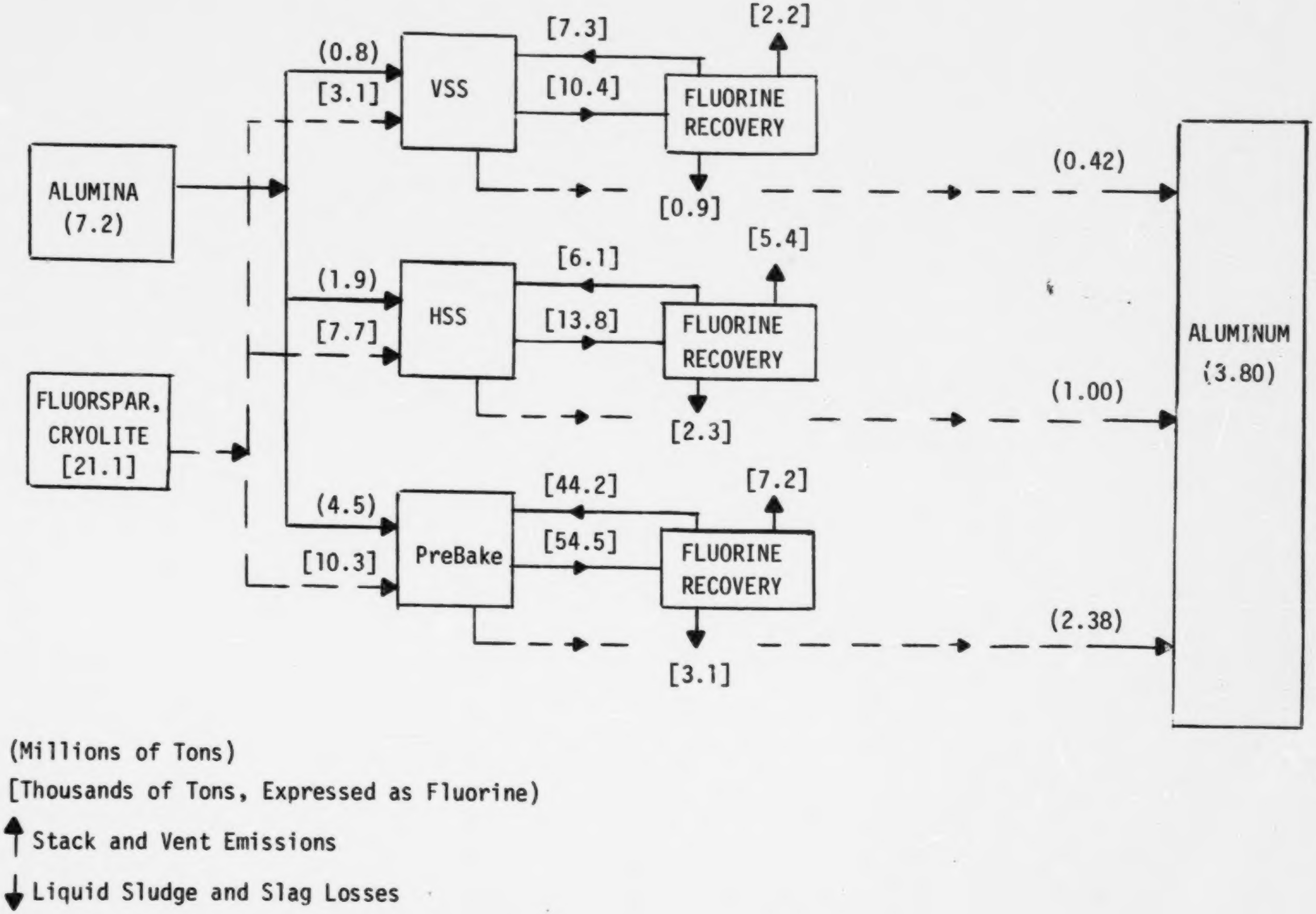

ALUMINA
(7.2)
FLUORSPAR,
CRYOLITE
[21.1]
(0.8)
[3.1]
VSS
[7.3]
[10.4]
FLUORINE RECOVERY
[2.2]
[0.9]
(0.42)
(1.9)
[7.7]
HSS
[6.1]
[13.8]
FLUORINE RECOVERY
[5.4]
[2.3]
(1.00)
(4.5)
[10.3]
PreBake
[44.2]
[54.5]
FLUORINE RECOVERY
[7.2]
[3.1]
(2.38)
ALUMINUM
(3.80)
(Millions of Tons)
[Thousands of Tons, Expressed as Fluorine)
↑ Stack and Vent Emissions
↓ Liquid Sludge and Slag Losses

FIGURE 1 SCHEMATIC SKETCH OF UNIT PROCESSES AND PER ANNUM MATERIALS FLOW AND FLUORIDE EMISSIONS IN THE PRIMARY ALUMINUM INDUSTRY

An aluminum reduction potline is a very large-scale operation. The individual pots are about 16 feet long, 8 feet wide and 6 feet deep. They are arranged side by side in the pot building which is of open high bay construction. It must be very well ventilated to dissipate the substantial heat of reaction; ventilation is achieved by a roof monitor that runs the length of the building.

In recent years, with increasing emphasis on control of fluorine emissions, the pots are operated with hoods designed to collect and control fluoride emissions. Because of the required pot mobility, however, it is extremely difficult to fabricate hoods which fit tightly and operate satisfactorily.

There are several sources of serious fluoride contamination. Fluorides are continually carried off by entrainment in the substantial quantities by the CO_2 evolved from the refining reaction. A second major source of contamination occurs during "crust breaking," an operation conducted from time to time to break up the frozen layer of alumina. In addition, the pots must be periodically stirred to maintain uniform concentrations in the bath and to keep the alumina ore in contact with the top of the bath. During such an operation, it is not possible to efficiently collect the evolved gases in the hood system, and the gases escape to the atmosphere of the building. A similar problem exists whenever an electrode must be changed and is even more serious than crust breaking because more of the hood must be removed to get at the electrode.

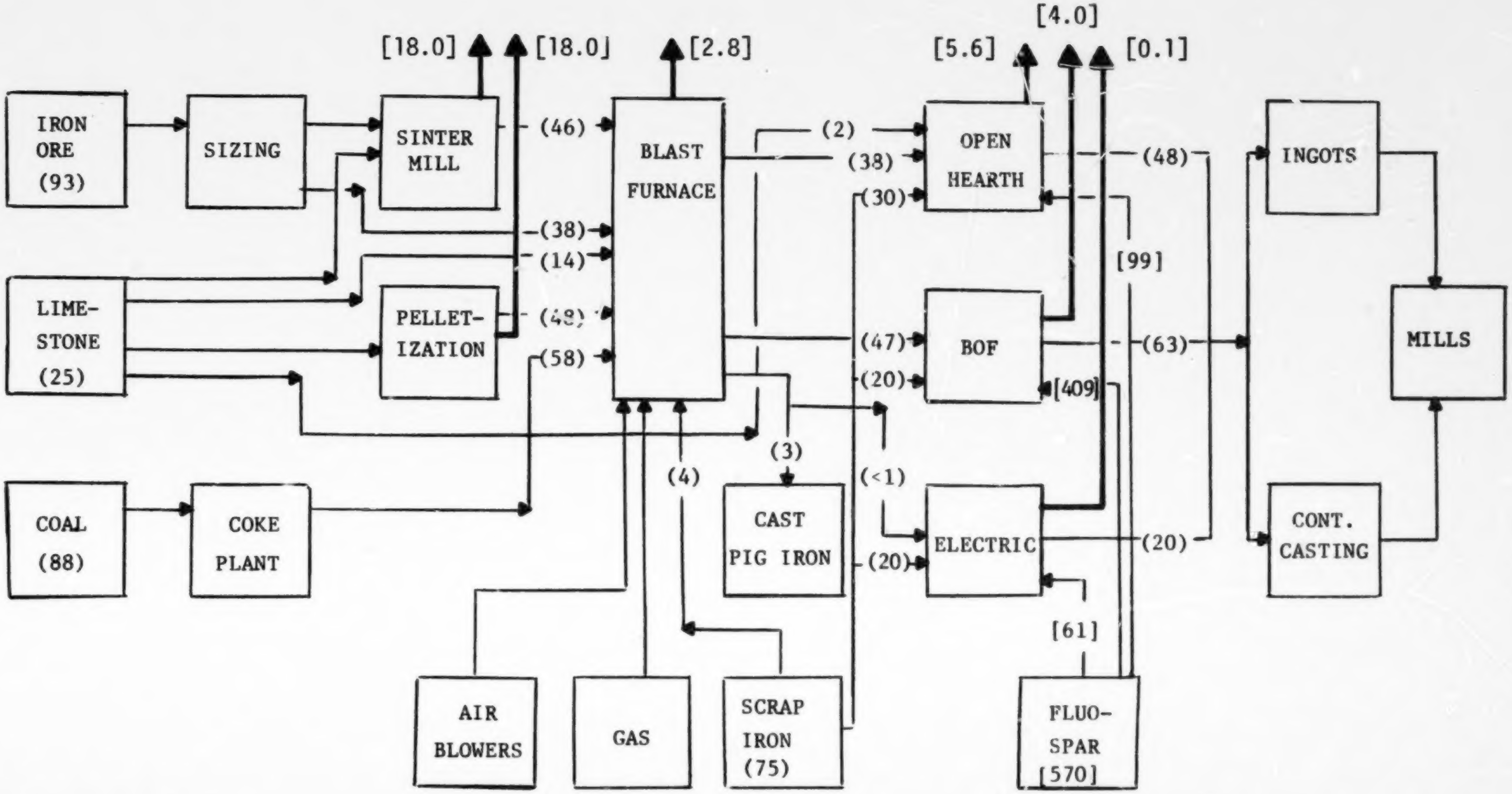
A major portion of fluorine emissions can be recovered by passing the gases collected in the hoods to a wet scrubbing system. Recovery of fluorine from the building atmosphere is a much more difficult problem. The quantity of gas to be scrubbed is of course very much larger than that collected by the hoods, and a number of roof scrubbers must be installed. Recently developed high efficiency control methods based on adsorption of fluorides onto the incoming alumina feed, such as the Alcoa 398 Process(2) which incorporates a fluid bed reactor, may be appropriate for cleaning roof monitor gases as well as hood gases.

Fluoride emissions can be as high as ten pounds per ton of aluminum produced.(1) Particulate emissions include Al_2O_3, carbon soot, Na_3AlF_6, AlF_3 and $Na_5Al_3F_{14}$. The major gaseous species are CO_2, CO, organic species (from the binders in the anode paste) and HF, which results from the hydrolysis of AlF_3 and, to a lesser extend, Na_3AlF_6. In addition, $NaAlF_4$ is a volatile specie, but it readily decomposes to $Na_5Al_3F_{14}$ and AlF_3.

2. Iron and Steel A typical steel mill emits 0.2 to 1 pound of fluorine (as fluorides) to the atmosphere per ton of steel produced. About 5 to 10% of the emitted fluoride is solid particulate and the remainder is gaseous.

The principal source of fluoride is fluorspar, CaF_2, which is employed in quantities of 2 to 15 pounds per ton of steel produced. The fluorspar is added as a slag conditioner to improve the collection of oxide impurities; the resulting increase in slag fluidity promotes desulfurization and increases the rate of heat transfer through the slag, improving process efficiency. Western ores, particularly those from southern Utah, include another source of fluoride. These ores contain 2,000 to 4,000 ppm fluorine present as fluorapatite, fluorspar and fluorosilicates. The remaining quantities of input fluorine are introduced as impurities in the other raw materials.

An integrated steel mill is comprised of several combined facilities, including a sintering plant, blast furnaces, coke and by-products plant and several steel making shops which utilize open hearth, electric and basic oxygen (BOF) furnaces. Support services are also required, including boiler plants, furnace and annealing rooms, scarfing areas, water treatment, etc. Each of these facilities contribute to pollution emissions to some extent. The major fluoride emissions result from iron ore pelletizing and sintering, and open hearth and BOF steelmaking processes. A flow diagram of an integrated steel mill operation showing raw material requirements and evolved fluorides is presented in Figure 2.


[18.0]
[18.0]
[2.8]
[5.6]
[4.0]
[0.1]
IRON ORE (93)
SIZING
SINTER MILL
LIME-STONE (25)
PELLET-IZATION
COAL (88)
COKE PLANT
(46)
(38)
(14)
(48)
(58)
BLAST FURNACE
(4)
(2)
(38)
(30)
(47)
(20)
(3)
(<1)
(20)
CAST PIG IRON
OPEN HEARTH
BOF
ELECTRIC
[99]
[409]
[61]
(48)
(63)
(20)
INGOTS
CONT. CASTING
MILLS
AIR BLOWERS
GAS
SCRAP IRON (75)
FLUO-SPAR [570]

[Thousands of Tons]
(Millions of Tons)
↑ Points of Fluoride Emissions

FIGURE 2 SCHEMATIC SKETCH OF UNIT PROCESSES AND PER ANNUM MATERIALS FLOW AND FLUORIDE EMISSIONS IN AN INTEGRATED STEEL MILL

a. Pelletizing and Sintering

Pelletizing and sintering are methods for recovering iron ore "fines" that would otherwise be lost as dust and converting them into a product suitable for charging into the blast furnace. Pelletization generally occurs at the mine whereas sinter shops are integral with a blast furnace. Both processes are similar and involve burning a mixture of ore-bearing fines and an appropriate fuel, such as coke breeze or blast furnace off-gases. Emissions consist almost entirely of particulates extrained in the combustion gases, which are large in volume. The sintering process is effective in removing sulfur from the charge so that sulfur oxides also occur in the off-gases. Other species present in small quantities include hydrocarbons, nitrogen oxides and fluorides. The fluorides are largely confined to operations utilizing Western ores, particularly those from southern Utah, which contain 0.02 to 0.04% mineral fluoride. In general, the fluoride emissions from pelletizing and sintering can be kept very low through addition of limestone to the sinter mix, which ties up much of the emitted fluoride in a slag.

b. Blast Furnace

Ore is reduced to iron in the blast furnace. The charge consists of iron ore, coke and limestone which are added at the top of the furnace. To promote combustion, a high volume of pre-heated air is forced up through the furnace. A series of deoxidation reactions occur as the charge descends down the furnace until finally, near the bottom of the furnace, a molten pool of reduced iron is formed covered by a slag containing many of the impurities. The process is continuous, with pig iron and slag being tapped off periodically.

Any fluorine that enters the blast furnace as a constituent of the ore, fuel or limestone will probably react with the limestone and leave the furnace with the slag. Gases from the blast furnace are collected, passed through stoves for heat recovery, and when reasonably cool, are passed through dust control equipment, which removes most of the adsorbed fluoride gas. The gas is then burned to recover remaining latent heat. Any gaseous fluorides remaining will be emitted to the atmosphere.

c. Steelmaking

Steelmaking involves a refinement of pig iron to reduce carbon and silicon content to the desired level and to remove or control other impurities. This refinement is carried out by heating a charge of pig iron, scrap and fluxing agents (limestone and fluorspar) in the presence of air. Carbon, silicon and manganese are oxidized and are either evolved in the off-gases or are collected in the slag. Three basic steelmaking processes are used--open hearth, basic oxygen (BOF) and electric, the latter of which is charged completely with steel scrap.

Open hearth operations are declining rapidly due to increased capacity for basic oxygen and electric steel. The BOF method has become increasingly important during the last decade as low cost supplies of oxygen have become available through improvements in cryogenic technology; steel refinement can be accomplished in 20 to 40 minutes compared with 8 to 12 hours required for the open hearth process. In addition, modern procedures for improving the quality and form of scrap are resulting in an increased production of electric furnace steel.

In U.S. practice, fluorspar consumption in open hearth steelmaking may range from zero up to 10 pounds of fluorspar per ton of steel, with an overall average consumption of about four pounds of spar per ton of steel. More fluorspar is used in making high-carbon heats, because the bath temperature and iron oxide content of the slag are generally lower for these heats. Furnaces operating with oxygen lancing generally consume less fluorspar, due to the higher bath temperature and stronger boil which greatly accelerate the shaping of the slag.

The addition of fluorspar causes the slag to become more fluid, thinning the "heavy slag" and facilitating the solution of lumps or "floaters." The effect of fluorspar on the slag is only temporary, lasting roughly one hour. About one percent of the calcium fluoride reacts with the silica according to the following reaction:

$$2\ CaF_2 + SiO_2 \rightarrow SiF_4 + 2\ CaO$$

This reaction increases the lime content and decreases the silica content, thereby increasing the effective activity of the lime to remove sulfur. While this reaction occurs only to a small extent, it does create an emission problem due to the fact that the SiF_4 volatilizes. There is also the possibility of direct reaction of fluorine on the sulfide to form SF_6. This would eliminate some of the sulfur in the slag, throwing the equilibrium between sulfur in the slag and in the metal out of balance. Further elimination of sulfur from the metal would then occur to maintain equilibrium. The presence of moisture in the combustion gases will tend to hydrolyze any SiF_4 to HF at the slag surface. In addition, there is an opportunity for direct pyrohydrolysis of any CaF_2 floating on the surface of the bath or carried into the gas stream as dust. There is also some evidence that magnesium forms stable slag constituents that reduce the tendency of fluoride to leave the slag system. Not only is the volatilization of SiF_4 suppressed but the pyrohydrolysis of magnesium fluoride (MgF_2) itself is insignificant up to 1300°C. Calcium does not appear to exert as strong an influence in reducing the tendency of fluorine to volatilize.

In comparison to the open hearth process, basic oxygen steelmaking is quite recent in development, accounting for less than 1 percent of the steel produced in 1960. The majority of new steelmaking installations, however, have been BOF, and basic oxygen steelmaking surpassed the open hearth in annual tonnage in 1970. The BOF smelting process is carried out in refractory lined cylindrical vessels that can accommodate from 50 to 250 tons of hot metal and scrap per charge. To speed up refinement, a stream of oxygen is impinged onto the liquid metal surface which results in violent agitation and intimate mixing of the oxygen with the molten iron. BOF steelmaking employs 12 to 15 pounds of CaF_2 per ton of steel, four to five times the amount used in open hearth.

The majority of the fluoride is tied up in the slag; emissions to the atmosphere are only a few percent of the fluoride input. It is postulated, however, that a considerable portion of the HF generated by slag reactions is adsorbed on the fine Fe_2O_3 dust that is blown from the furnace.

Finally, electric furnace steelmaking utilizes anywhere from 3 to 15 pounds of CaF_2 per ton of steel, with an average of 8 pounds. Since there is only a moderate gas input to the electric furnace, hoods and vents can be effectively employed for collecting and controlling particulate emissions.

3. Glass Glass processing produces emissions to the atmosphere through physical entrainment in the air stream flowing through the glass-making furnace and by volatilization from the molten glass. The major effluent species are fluorides, silicates, sulfates and borates. Fluoride emissions are generally restricted to the production of specialty glasses, including opals, technical grade products and leaded glasses. Major fluoride species include gaseous SiF_4, HF and F_2 as well as PbF_2, NaF and CaF_2 particulate. A schematic sketch of the glassmaking processes as well as a materials flow chart and fluoride emissions is presented in Figure 3.

Glass manufacturing involves a high temperature conversion of raw materials into a homogeneous melt. Principal raw materials include sand, feldspar, soda ash and limestone; in addition, many other elements are utilized in small amounts in the manufacture of specific glass compositions.

With few exceptions, the major amounts of glass produced in the U.S. are melted in continuous tanks with capacities up to 300 tons per day. Furnaces are fired by natural gas or oil fuels and, to a lesser extent, by electric melting. Glass melting furnaces and tanks are usually provided with regenerators to recover heat from the flue gas before it passes out the stack. Reactions between the component raw materials and

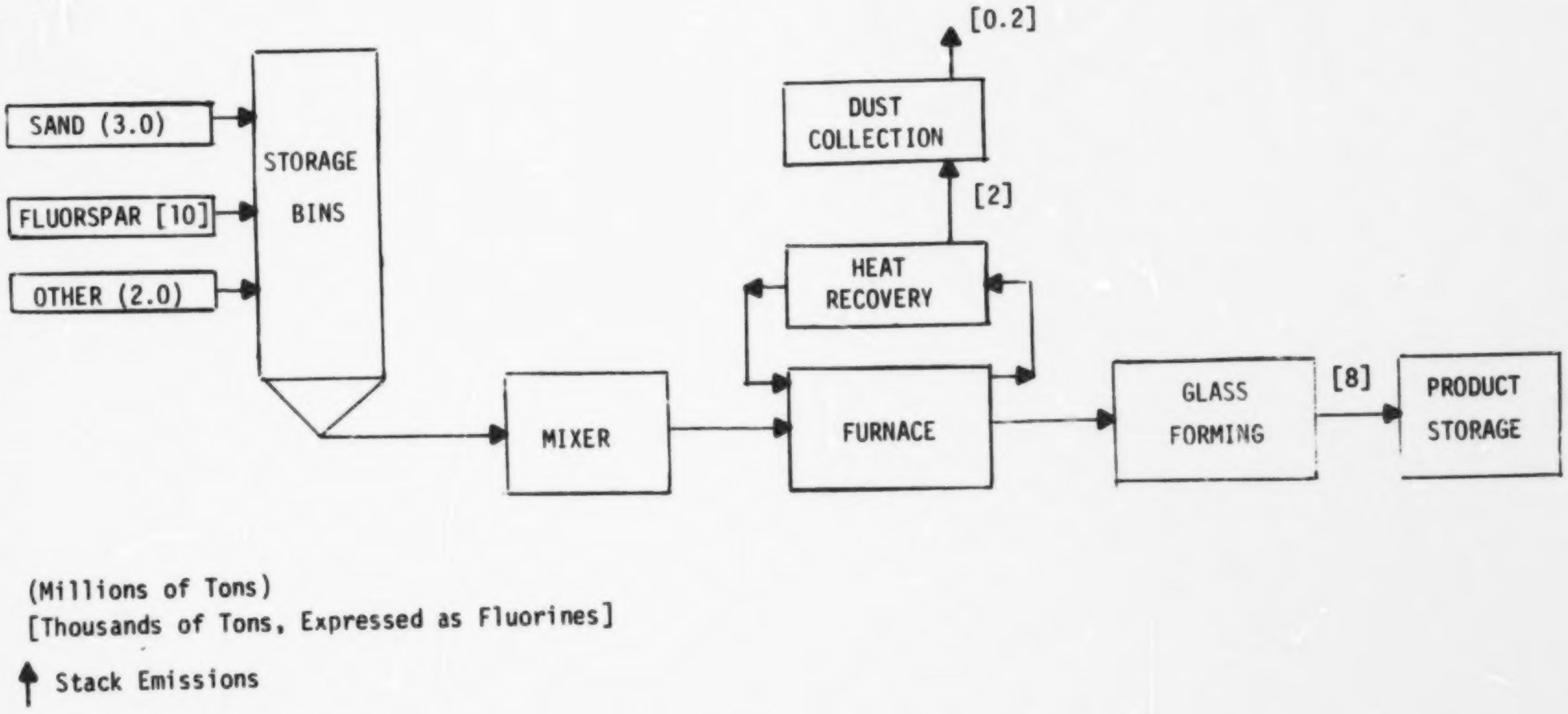

[0.2]
DUST COLLECTION
[2]
HEAT RECOVERY
SAND (3.0)
FLUORSPAR [10]
OTHER (2.0)
STORAGE BINS
MIXER
FURNACE
GLASS FORMING
[8]
PRODUCT STORAGE
(Millions of Tons)
[Thousands of Tons, Expressed as Fluorines]
Stack Emissions

FIGURE 3 SCHEMATIC SKETCH OF UNIT PROCESSES AND PER ANNUM MATERIALS FLOW IN GLASS MANUFACTURING

the volatilization of the batch in the glass tank account for the emission of sulfur dioxide, carbon dioxide, nitrous oxides, fluorides, etc., in the stack emission. Fluoride compounds are often used as a source of sodium, lithium and calcium. In addition, these compounds serve as fluxes to enhance melting and as fining agents to improve homogeneity and remove bubbles. Crystalline precipitates of CaF_2 provides the opacity characteristic of the opal glasses. This latter process is the major source of fluoride emissions in the glass making industry.

4. Phosphate Rock Processing Some 25 million tons of phosphate rock is processed annually in the United States. The rock is mostly fluorapatite $[3Ca_3(PO_4)_2 \cdot CaF_2]$ and hydroxyapatite $[3Ca_3(PO_4)_2 \cdot Ca(OH)_2]$; the fluoride content is generally 3 to 4% on a weight basis. Approximately one third of the rock is processed into phosphoric acid (by the wet process method) and a quarter is used for electric furnace production of elemental phosphorous and phosphoric acid. The remaining 40% is used mainly in the production of fertilizers, including triple superphosphate (TSP), normal superphosphate (NDP), diammonium phosphate (DAP), and dicalcium phosphate, and defluorinated rock which is employed in feed preparations for cattle and chickens.

A schematic sketch of the various process operations and corresponding levels of fluoride emissions is presented in Figure 4. Most of the phosphoric acid produced by the wet process is subsequently used in other processes, including the preparation of TSP and DAP. The major fluoride emissions from all of these processing operations are HF and SiF_4; the latter readily hydrolyzes to H_2SiF_6. The various operations are briefly summarized below.

a. Wet-Process Phosphoric Acid

In the wet process, reaction of phosphate rock with an acid produces free phosphoric acid and the salt of the acid. In most commercial processes, sulfuric acid is used; the by-product salt is calcium sulfate which precipitates as gypsum and is removed by filtration. The reaction is described by the following equation:

$$3Ca_{10}(PO_4)_6F_2 + 30H_2SO_4 + SiO_2 + 58H_2O \rightarrow 30CaSO_4 \cdot 2H_2O + 18H_3PO_4 + H_2SiF_6$$

There are a number of impurities in the phosphate rock which consume acid and affect the reaction. One of the principal impurities is fluoride. Generally, it is present in either of two forms—as part of the fluorapatite mineral and as additional amounts of free calcium fluoride. When the rock is acidified, fluoride is converted to hydrofluoric acid. In most rocks, there is enough silica present to react with all of this hydrofluoric acid. In most rocks, there is enough silica present to react with all of this hydrofluoric acid to form fluosilicic acid. At the temperatures and acidity conditions under which the digestion reaction must be carried out, some of the fluosilicic acid is vaporized as silicon tetrafluoride gas with traces of gaseous hydrofluoric acid.

In most plants, the substantial heat of reaction is removed by sparging the digester with air or by flash cooling of the hot liquor. In either case, there is substantial emission of air, steam, the fluorine containing gases, and P_2O_5 mist to the stack. The effluent gas is processed in a wet scrubber in which the fluorine compounds and the P_2O_5 are absorbed in water to make dilute solutions. In some plants fluorine containing by-products are recovered from the scrubber liquor. In most cases, however, the liquor is discharged as an effluent by way of the gypsum disposal pond and acid water cooling ponds.

b. Elemental Phosphorus

In the production of elemental phosphorus, phosphate rock is reacted in an electric furnace with silica and coke, according to the formula $2Ca_3(PO_4)_2 + 6SiO_2 + 10C \rightarrow 6CaSiO_3 + P_4 + 10CO_2$

The volatized phosphorus is carried along by the gas stream, which is mostly CO and CO_2 and is condensed. Iron present in the phosphate rock is reduced to the elemental form and alloys with the phosphorus to form a ferrosphosphorus by-product. The furnace effluent also contains nitrogen, hydrogen, methane, and fluorides. Particulate matter entrained in the

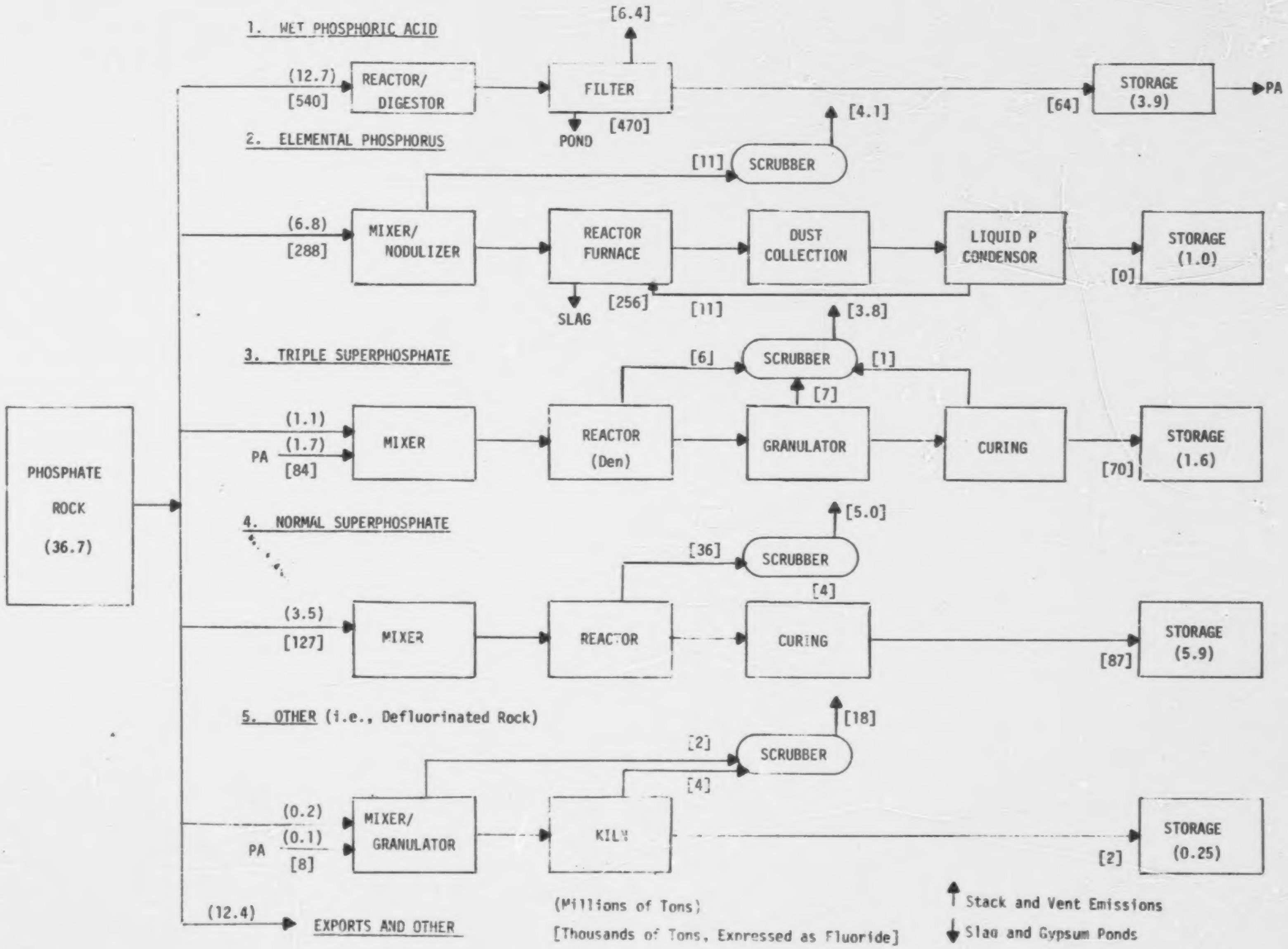

1. WET PHOSPHORIC ACID
(12.7)
[540]
REACTOR/ DIGESTOR
[6.4]
FILTER
POND
[470]
[64]
STORAGE (3.9)
PA
2. ELEMENTAL PHOSPHORUS
[11]
SCRUBBER
[4.1]
(6.8)
[288]
MIXER/ NODULIZER
REACTOR FURNACE
SLAG
[256]
[11]
DUST COLLECTION
LIQUID P CONDENSOR
[0]
STORAGE (1.0)
3. TRIPLE SUPERPHOSPHATE
PHOSPHATE ROCK (36.7)
(1.1)
PA
(1.7)
[84]
MIXER
REACTOR (Den)
[6]
SCRUBBER
[3.8]
[7]
[1]
GRANULATOR
CURING
[70]
STORAGE (1.6)
4. NORMAL SUPERPHOSPHATE
(3.5)
[127]
MIXER
REACTOR
[36]
SCRUBBER
[5.0]
[4]
CURING
[87]
STORAGE (5.9)
5. OTHER (i.e., Defluorinated Rock)
(0.2)
PA
(0.1)
[8]
MIXER/ GRANULATOR
KILN
[2]
[4]
SCRUBBER
[18]
[2]
STORAGE (0.25)
(12.4)
EXPORTS AND OTHER
(Millions of Tons)
[Thousands of Tons, Expressed as Fluoride]
Stack and Vent Emissions
Slag and Gypsum Ponds

FIGURE 4 SCHEMATIC SKETCH OF UNIT PROCESSES AND PER ANNUM MATERIALS FLOW IN THE PHOSPHATE ROCK PROCESSING INDUSTRY

furnace gases is collected by a precipitator and returned to the furnace.

The phosphate rock generally undergoes treatment prior to being fed to the electric furnace. The most common method of treatment is nodulizing the phosphate rock in a rotary kiln at a temperature of 1200° or more in which the rock is heated to the point of incipient fusion and agglomerated. During this nodulizing operation, organic matter, moisture, carbon dioxide and part of the fluoride are removed.

c. Triple Superphosphate (TSP)

A principal end product of the phosphate fertilizer industry is triple superphosphate, which is a solid product formed by acidulating phosphate rock with phosphoric acid. For run-of-pile triple, 50% P_2O_5 acid and ground rock are mixed and the product, which is a pasty mass, is conveyed to storage, where reaction or "curing" continues along with drying. The product is subsequently removed, crushed, screened and shipped as a sized solid. This simple process, however, is difficult to control because of the process conditions and the nature of materials. Therefore, careful attention to fume control is required. The principal contaminants are gaseous fluorides and phosphate rock dust. All of the equipment must be closed or hooded and vented to a stack through suitable fume control equipment, which is commonly some type of one- or two-stage wet scrubber.

A special problem exists in the storage building where substantial quantities of gaseous fluorides are evolved during the curing of the triple superphosphate. To control this fume, the ventilating air must be collected and passed through a scrubber.

d. Normal Superphosphate (NSP)

Normal superphosphate is formed by the reaction of phosphate rock with sufficient sulfuric acid to convert the phosphate ore to monocalcium phosphate. The sulfuric acid is tied up in the process as calcium sulfate. Since the P_2O_5 content of NSP is only about 20% compared to 45-50% in TSP, demands for this product are falling off.

There is a great variety of equipment in use for manufacture of normal superphosphate. The older plants were batch-type units; some of the newer plants operate in a continuous manner and are equivalent to the system used for triple superphosphate. Equipment required includes a heavy duty mixer to contact the finely ground phosphate rock with sulfuric acid, and then a means for discharging the partially reacted mass to a storage area where completion of the reaction and drying can occur. The evolution of steam, CO_2, and the air required for ventilation results in substantial emissions of gaseous fluorides containing fume and rock dust. The appreciation of the need to control these emissions came much later than the establishment of the plants and the adoption of control devices varies widely throughout the industry.

e. Ammoniated Phosphate

In addition to phosphate, a complete fertilizer must also contain, among other elements, nitrogen which can be in either the ammoniacal, nitrate, or urea form. Such materials are manufactured by mixing and reacting ammonia or nitrogen solutions with phosphoric acid or with triple superphosphate. The degree of conversion can be to either monoammonium phosphate or to diammonium phosphate. Diammonium phosphate is preferred in today's market because of its higher total plant food analysis. In many plants, particularly at midwest locations remote from the primary phosphoric acid facilities, the preferred method is to react ammonia and nitrogen solutions with triple superphosphate. In this reaction, part of the monocalcium phosphate is converted to dicalcium phosphate; the monoammonium phosphate so formed can be further converted to diammonium phosphate. Ammonium nitrate or urea can also be present in these ammoniating solutions and upon drying, remain with the fertilizer material and fortify its plant food content. A substantial portion of the fluorine present in the original phosphate rock is present in the phosphoric acid or the triple superphosphate used for the ammoniation reactions. In the reaction and drying step, appreciable quantities of this fluorine are driven off as silica tetrafluoride together with ammonia gas and must be handled in a vent and scrubber system. The drying and screening operations are very dusty and this dust is recovered in cyclones which are part of the vent system. Wet scrubbers commonly employed after the cyclones are of the vent system. Wet scrubbers commonly employed after the cyclones are of the venturi or the cyclonic contact type. There is wide variation in the efficiency of these emission control devices in the industry.

f. Defluorinated Phosphate Rock

The animal feed industry requires supplements of phosphorus in their feed preparations, primarily those for cattle and chickens. The major source of this phosphorus today is from defluorinated phosphate rock which is low in cost and readily available from phosphate processors. Fluoride content of the rock used in animal feed preparations must be reduced to about 0.2% fluoride for safe use.

The process used by several producers today consists of mixing preweighted portions of phosphate rock, wet process phosphoric acid, and sodium carbonate. The mixture is fed into a counter-current high temperature kiln or a high temperature fluid bed calciner. Gases from the kiln or calciner contain essentially all of the fluorine in the phosphate rock and phosphoric acid feed and dust. Multiple stage wet scrubbers are used to remove the fluorides as a weak hydrofluoric acid solution which is neutralized or disposed of by other means.

g. Dicalcium Phosphate

As an alternative to the process described above, some dicalcium phosphate for animal feed supplements is produced by the reactions of defluorinated phosphoric acid with lime. A relatively dilute acid solution is neutralized to the dicalcium stage with a slurry of lime. The operation is carried out batch-wise and the heat of reaction removes essentially all of the water leaving a thick paste. This paste is then dried, the limps broken up and the product packaged for use.

Aside from particulate air pollution problems arising from the handling of the lime and the dried product, the principal source of pollution stems from the defluorination of wet process acid used in the process. This defluorination is often accomplished by the addition of a reactive form of silica such as diatomaceous earth to the crude acid and then the injection of steam to help volatilize the contained fluorine. The fluorine evolved from the acid is collected in wet scrubbers.

C. Summary of Emission Species

A review of the various emission species associated with each of the stationary source industries considered here are presented in summary form in Table 1. The principal gaseous fluoride species are HF and SiF_4, both of which are highly soluble and are easily collected in water. Other gaseous species that would be collected at the same time include SO_3 (and maybe some NO_2 and SO_2). A variety of particulate fluorides can be entrained in process effluents. These depend largely on the raw materials utilized in the unit process operations. In general, fluorspar (CaF_2) is the most prevalent fluoride particulate specie in the glass and steel industries. Similarly, fluorapatite [$Ca_{10}(PO_4)_6F_2$] and cryolite (Na_3AlF_6) are the major fluoride particulate species in the phosphate rock processing and primary aluminum industries, respectively.

Table 1

Summary of Gaseous and Particulate Emission Species from Stationary Source Industries

Industry	Emission Species			
	Gaseous fluorides	Other gases	Particulate Fluorides	Other Particulate
Primary Aluminum	HF	CO_2, CO, hydrocarbons	Na_3AlF_6 AlF_3 $Na_5Al_3F_{14}$	Al_2O_3 Carbon soot
Iron and Steel	HF,SiF_4	CO_2,CO,NO_x SO_2,SO_3,O_2	CaF_2	Fe_2O_3,FeO MnO,SiO_2, CaO,Na_2O
Glass	SiF_4,HF,F_2, BF_3,H_2SiF_6	SO_2,SO_3,CO, Cl,NO_x	CaF_2,NaF Na_2SiF_6,PbF_2	SiO_2,PbO CaO,Na_2SO_4
Phosphate Rock				
--Acidulation	HF,SiF_4,F_2	SO_2,SO_3	$Ca_{10}(PO_4)F_2$, CaF_2	P_2O_5, $CaSO_4 \cdot 2H_2O$
--Electric Furnace		P_5,CO,CH_4, N_2,H_2,CO_2	$Ca_{10}(PO_4)_6F_2$,	SiO_2

IV. Sample Collection

A. Introduction

The greatest drawback to the reliable collection of fluoride emission samples from stationary sources is the pronounced chemical reactivity of most fluoride compounds, especially HF. This is especially important in light of the fact that fluoride levels in reasonably controlled emissions are typically in the range of 0.1 to 5 parts per million (ppm). Any reaction of fluoride with the sample collection equipment or storage containers could greatly influence the accuracy of the measurement.

Because of the substantial differences in the raw materials and manufacturing operations employed in the stationary source industries that are being considered, and furthermore, within the various unit processes of each industry, there are considerable variations in the makeup of the stack emissions. It is necessary, therefore, to know as closely as possible the types of species that are typically present in the stack stream as well as their physical and chemical properties, such as particle size, solubility and gas adsorptivity, so that appropriate stack sampling procedures and equipment can be employed. Additionally, the analytical requirements have a major impact on sample collection procedures. For example, the apparatus and procedure to collect a sample for "total soluble fluorides" would undoubtedly be much simpler than a requirement for separate gaseous fluoride, soluble particulate fluoride and insoluble particulate fluoride analyses. Consideration should also be given to ancillary information that can be obtained from the collected samples. It should be possible, in most cases, to measure "total particulate" in addition to the required fluoride analyses. In addition to emitted species, consideration must also be given to the physical condition of the effluent stream, including stream velocity, homogeneity, temperature, relative humidity and so forth. A very wet stream, for example, may preclude the use of a filter for collecting particulate.

Two approaches have been suggested for dealing with the chemical reactivity of fluoride compounds. The classical approach is to employ "inert" materials, such as stainless steel, various plastics and epoxies and elastomers. However, a sampling system which appears to be "inert" to one gas stream may, in fact, be highly reactive to another due to a change in the chemistry of the emission species, temperature or humidity. An alternate approach is to design the sampling apparatus so that all gaseous fluorides are intentionally converted to a known, collectable, relatively stable form. This approach has been applied by employing a heated glass probe which presumably converts all HF and other gaseous fluorides to H_2SiF_6 which is highly soluble in water and is efficiently collected in a liquid impinger. However, conversion efficiencies have not been determined for the complete range of conditions which would be encountered in the various industries and processes of concern.

Finally, after stack samples have been collected, it is necessary to assure that there is no change in chemistry during the storage period prior to analysis. As a result, it is necessary to establish suitable procedures for sample transit and storage.

The remaining portion of this section presents a review of fluoride stack sampling procedures given in the open literature; a discussion of procedures and equipment employed by representative companies within the primary aluminum, steel, phosphate rock processing and glass manufacturing industries; a presentation of the results of some laboratory studies carried out to evaluate the effect of fluoride ion on sampling train materials of construction and on sample container materials; and finally, our recommendations for tentative sampling methods to be evaluated in an anticipated field study. As used herein, "dry" streams are those having a relative humidity of less than 100% at stack conditions, whereas "wet" streams imply the physical entrainment of water (or steam) in the stream.

B. Review of Sample Collection Procedures and Equipment

In terms of measuring the fluoride emissions from stationary sources, the principal function of the sampling apparatus is to accurately and reproducibly carry out the collection and separation (where possible) of gaseous and particulate fluoride species in the presence of other process emissions. Only a few studies addressing this subject have appeared in the open literature. These studies have employed apparatus designed for the collection of total particulate, such as the so-called PHS (currently designated EPA) sampling train developed by W.S. Smith.(3) The apparatus, shown schematically in Figure 5, consists of a heated glass probe (3), cyclone (4), and filter (5); water inpingers (8-11); and a dry gas meter (19), vacuum pump (17) and flow meter (20).

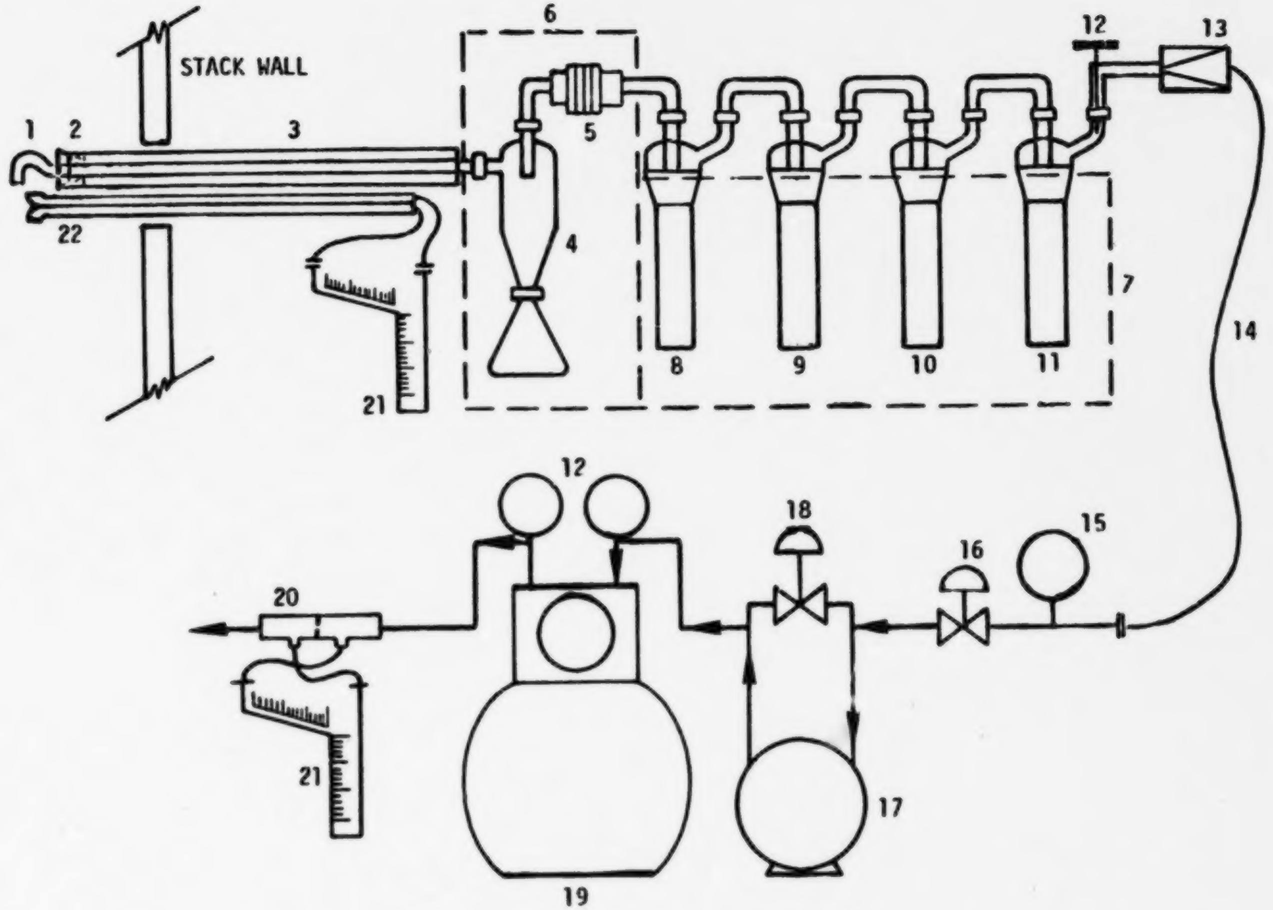
1. Glass Probe Sampling Apparatus

Dorsey and Kemnitz(4) found overall fluoride collection efficiencies of near 100%; however, in the case of experiments utilizing the lowest range of HF concentration (0 to 0.4%), collection efficiencies were only about 90%. Because of the limited amount of data presented in this paper, it is difficult to judge the applicability of the "gaseous fluoride conversion" approach via a heated glass probe without further laboratory and field-based evaluations.

The fragility of the glass probe in field work, the conversion efficiency when the glass probe becomes coated by particulate dust or tarry organic species, and the formation of geletinaceous silica hydrate during the hydrolyzation of SiF_4 which may plug the impingers are additional factors that must also be considered for this type of system.

2. Inert Probe Sampling Apparatus

The only other stack sampling procedures for fluorides reported in the literature(6,7) rely on the utilization of "inert" sampling equipment. Heated components, including probes, cyclones and filter holders, are generally constructed from 316 stainless steel; other components, such as impinger bottles and connectors, are made of polyethylene or polypropylene. No data has been presented on the efficiency of these systems.



STACK WALL
1
2
3
22
21
6
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4
8
9
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16
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20
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19
17

FIGURE 5 P.H.S. PARTICULATE SAMPLING SYSTEM(3)

Numerous procedures have been employed for ambient air sampling of fluorides which, in some cases, may be applicable to stack sampling. The various ambient air sampling methods have recently been reviewed by Robinson, et.al(1) which updates previous reviews by Farrah(3) and Mandl, et.al.(9)

C. Present Industrial Practices

During the course of our study, we carried out discussions with representatives of one or more companies within each of the four industries to discuss present practice in fluoride emissions sampling and analysis. Three of the companies had been analyzing stack emissions for fluorides for over fifteen years, and the company with the least experience, for five years. As a result of this extensive experience, most of these companies feel that their methods for the detection of fluorides are reliable, accurate and well tested. There is a general reluctance to employ other procedures.

Insofar as was possible, the points raised in these discussions were directed to elicit the views of the industry in general and not necessarily those of the company to which we were talking. The following information was developed during these discussions.

1. Primary Aluminum Particulate emissions from the fused salt electrolysis cells employed in primary aluminum production consist almost entirely of alumina (Al_2O_3) and cryolite (Na_3AlF_6). These species exhibit a bimodal size distribution, with a 30μm dust and 0.1-0.3μm fume average. It is probable that both chemisorption and physical adsorption of HF onto particulate species occurs in the stack fume. As a result, chemical analysis of the fluoride distribution between gas and solid phases will generally be biased in favor of fluoride particulate.

Stack gas streams have temperatures of 100-200°F. As a result, it has been possible to use various plastics and elastomers that are highly inert to fluorides for sampling train components. One aluminum producer utilizes an epoxy paint-coated aluminum tube for a sampling probe; the epoxy provides chemical inertness and the aluminum imparts mechanical strength and is light weight. Polypropylene, polyethylene and viton were identified as being highly inert to humidified HF in laboratory evaluations carried out by this company and were recommended as construction materials for sampling apparatus components. Tygon tubing was found to degrade rapidly in HF and should be avoided even for short connections.

Typical sampling apparatus utilizes a stainless steel nozzle, epoxy-lined metal probe, heated filter and impingers. Whatman 32 filter paper has been found to be very efficient for collecting the fine particulate in the fume. Impingers are held in an ice bath and contain distilled water or dilute caustic scrubbing solutions to collect gaseous fluorides.

Sampling procedure includes isokinetic sampling at each of four to six points located along two diameters 90° apart at 0.5 to 1.0 cfm. Each point is sampled for 10 to 15 minutes, resulting in a total sampling time of 2 hours.

2. Steelmaking Iron oxide dust is the major particulate emission from most steelmaking processes. Although there are some fluoride particulates, most of the emitted fluoride is gaseous. Stack gases are usually dry and, at the point of sampling, have temperatures of 200-300°F for an open hearth.

Several unpublished studies carried out by steelmaking companies have shown that iron oxide dust is an efficient collector for HF. Since particulate filters may therefore trap considerable quantities of HF in addition to the particulate, distribution between solid and gaseous fluorides could be greatly in error. One approach that has apparently worked well has been to employ an electrostatic precipitator in place of a cyclone and filter combination.(7) In this way, the surface area of the particulate is kept very small and gas-particulate reactions are minimized. Gaseous fluorides are collected in distilled water or dilute NaOH solutions.

Stainless steel (Type 316) and polyethylene sampling train components have been used over long periods of time (several years) with no evidence of degradation due to exposure to fluorides. This lack of reactivity may have resulted from the low water content in the gas stream. Glass components have not been used to date due to their potential adverse reactions, i.e., reaction of HF with glass to form a stable phase such as CaF_2. Furthermore, many operators consider glassware to be too fragile for practical use in the field.

Sampling is typically carried out at a single point of average velocity at a rate of about 1 cfm. The sampling rate is adjusted for cyclic operations to maintain gas velocity within 10% of average velocity. Sampling is usually carried out for one hour. The probe and particulate collector (precipitator or filter) is maintained at a temperature greater than the water dewpoint and the impinger solutions are held in an ice bath.

3. Glass Manufacturing Glass furnaces usually do not employ any anti-pollution control (APC) devices; control is effected by good operating practice. Stack temperatures can be as high as 1000°F, although 600°F is typical. Emissions can vary considerably, depending on the product being manufactured. There are greater fluoride emissions, for example, in the manufacturing of fiber glass as well as opal, borosilicate and leaded glasses. Except for PbF_2, the particulate fluorides are water soluble. The major gaseous fluoride specie is SiF_4, although HF, F_2 and BF_3 may also be present.

Stack sampling in the glass industry is generally carried out to monitor visible particulate, SO_2, SO_3 and fluorides. The company we visited utilized a sampling system consisting of a stainless steel probe and glass fiber filter (both heated to about 500°F to avoid SO_3 and water condensation) followed by an SO_3 condensor and several water impingers in an ice bath. The filter is often removed when samples are being collected for fluoride measurements alone, since all particulate fluorides (except for PbF_2) are soluble. Of course, in using this latter approach, one gets a total fluoride analysis, for it is impossible to distinguish between soluble particulate and gaseous fluoride fractions.

Sampling is generally carried out isokinetically at a single point of average velocity at a rate of 0.75-1.25 cfm. Tests usually cover two reversals in cycle of the heat regenerator system, requiring 50 to 80 minutes. Experimentation is being conducted by one company on the use of an in-stack particulate collector. Alundum thimbles were found to pass the fine particulate or, for smaller pore thimbles, to quickly become plugged and were therefore ruled out as a particulate collector. An in-stack glass fiber filter in a stainless holder is presently being evaluated. The advantage of in-stack collectors is to reduce the opportunity for gas-solid phase interactions and transformations within the cooler portions of the sampling apparatus, which would lead to a false analysis.

4. Phosphate Rock Processing A common characteristic of almost all of the processes that utilize phosphate rock is a very wet exhaust gas stream; most of the process streams carry entrained water droplets or contain large quantities of steam. As a result, particulate filters have not been used in stack sampling for even though they are heated, the amount of water entrainment is sufficient to cause plugging. Therefore, all of the particulate, as well as the soluble gaseous fluorides, are collected in the impingers, and analyses are limited to providing the total fluoride content.

Most phosphate rock processing companies employ the procedure adopted by the State of Florida for the sampling and analysis of water soluble fluorides in stack emissions.(6) A typical sampling train for use with this method consists of a stainless steel probe, two impingers in series containing 0.1N sodium hydroxide for the collection of fluorides, a dry impinger, a dry gas meter, and finally a vacuum pump. In some cases, a filter is included between the second impinger and the mist trap to collect any particulate or aerosol that passes through the impingers.

These filters consist of glass fiber filters, alundum thimbles or funnels packed with glass wool. A schematic representation of the equipment. which is also used for particulate analysis with the filter included, is shown in Figure 6.

Sampling is carried out isokinetically at the point of average velocity as long as there is a low concentration of material entrained in the stream. In cases where either wet or dry cyclones are employed, significant tengential stratification occurs in the stream and the samples are collected incrementally at a series of traverse points.

5. Summary of Methods Employed by Industry The primary aluminum, glass and steel industries all have "dry" emission streams and can therefore carry out separation of gaseous and particulate fluorides by straightforward methods. Several types of particulate collectors have been employed, apparently with good reliability, including electrostatic precipitators and high efficiency filters. The former tends to minimize particulate surface area which would be expected to reduce the potential for gaseous interactions with the collected particulate. Pre-treated filters have been used efficiently for some applications where only light particulate loadings are encountered. In either case, some of the particulate is generally collected along the walls of the sampling probe. Attempts have been made to reduce the amount of particulate in the probe by employing an in-stack filter; although there is insufficient data reported to demonstrate the effectiveness of this approach, further consideration appears to be warranted. All sampling trains employ impingers to collect gaseous fluorides. There does not appear to be any difference in the collection efficiency by water or dilute caustic

Phosphate rock processing operations are characterized by "wet" streams which generally preclude the use of a particulate collector before the impingers. Consequently, there is no provision for carrying out a separation of gaseous and water soluble particulate fluorides for this case. The apparatus generally used for sampling stack emission

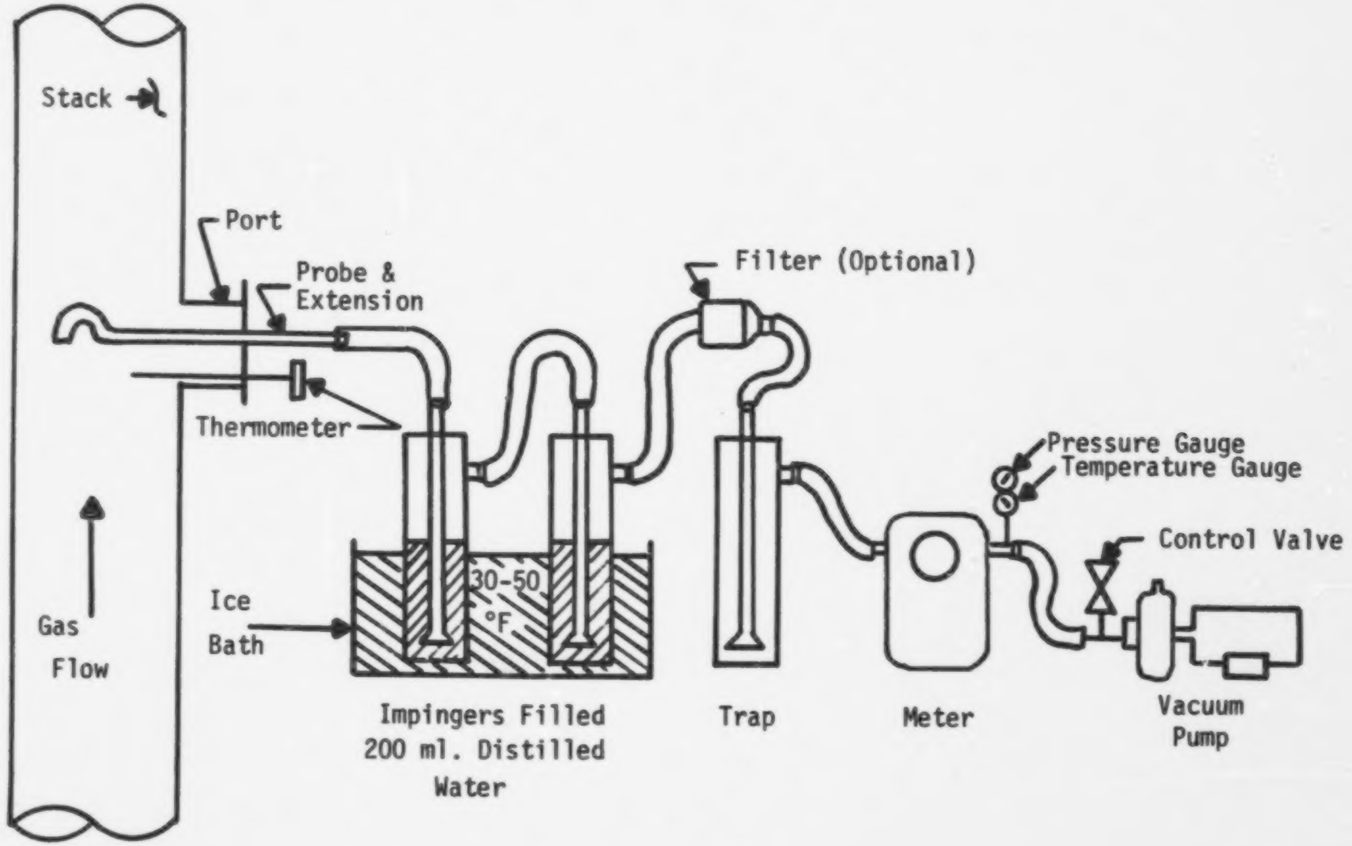
Stack
Port
Probe & Extension
Filter (Optional)
Thermometer
Pressure Gauge
Temperature Gauge
Control Valve
30-50 °F
Ice Bath
Gas Flow
Impingers Filled 200 ml. Distilled Water
Trap
Meter
Vacuum Pump

FIGURE 6. SCHEMATIC SKETCH OF WET-STREAM FLUORIDE STACK SAMPLING APPARATUS

is therefore the same as for the "dry" stream industries except for elimination of the particulate collector.

Sampling practice within all industries is reasonably uniform, involving single point isokinetic sampling for a sufficient length of time (30 minutes to 2 hours) to average the effect of process variations. In cases where there is good evidence for large variations in stream velocity from point to point, or for stratification or "cycloning," sampling is carried out along a point traverse. Collected samples are generally brought directly to the analytical laboratory or, when necessary, are stored and sealed in plastic containers.

D. Laboratory Evaluation of Sample Collection and Storage Materials

1. Evaluation of Sample Probe Materials There is uncertainty in the efficiency of hot glass probes for converting gaseous fluorides to SiF_4 at low fluoride concentrations. A study by Dorsey and Kenmitz$^{(4)}$ yielded an efficiency of about 90% for a range of concentrations from 0 to 0.4% HF in air at temperatures of 200 to 360°F. No measurements were made at the 0.1 to 20 ppm levels$^{(10)}$ which are likely to be found in stationary source emissions. Furthermore, the reported "inertness" of 316 stainless steel to gaseous fluorides has never been documented.

To aid in the selection of an appropriate material for sampling apparatus, a series of laboratory evaluations were carried out to evaluate the suitability of glass and 316 stainless steel as probe materials. A schematic sketch of the experimental apparatus is presented in Figure 7. Procedurally, nitrogen containing 1000 ppm HF was mixed with humidified air to provide concentrations within the range of 0.1 to 100 ppm HF. This stream was then preheated in a furnace coil to a temperature within the range 100 to 350°F in simulation of stack conditions. The stream was then split, with equal gas volumes passing through both legs of a Tee, as determined by calibrated flow meters. One branch of the Tee passed directly to a series of two impingers while the other branch passed through a 5-foot length of the sample material

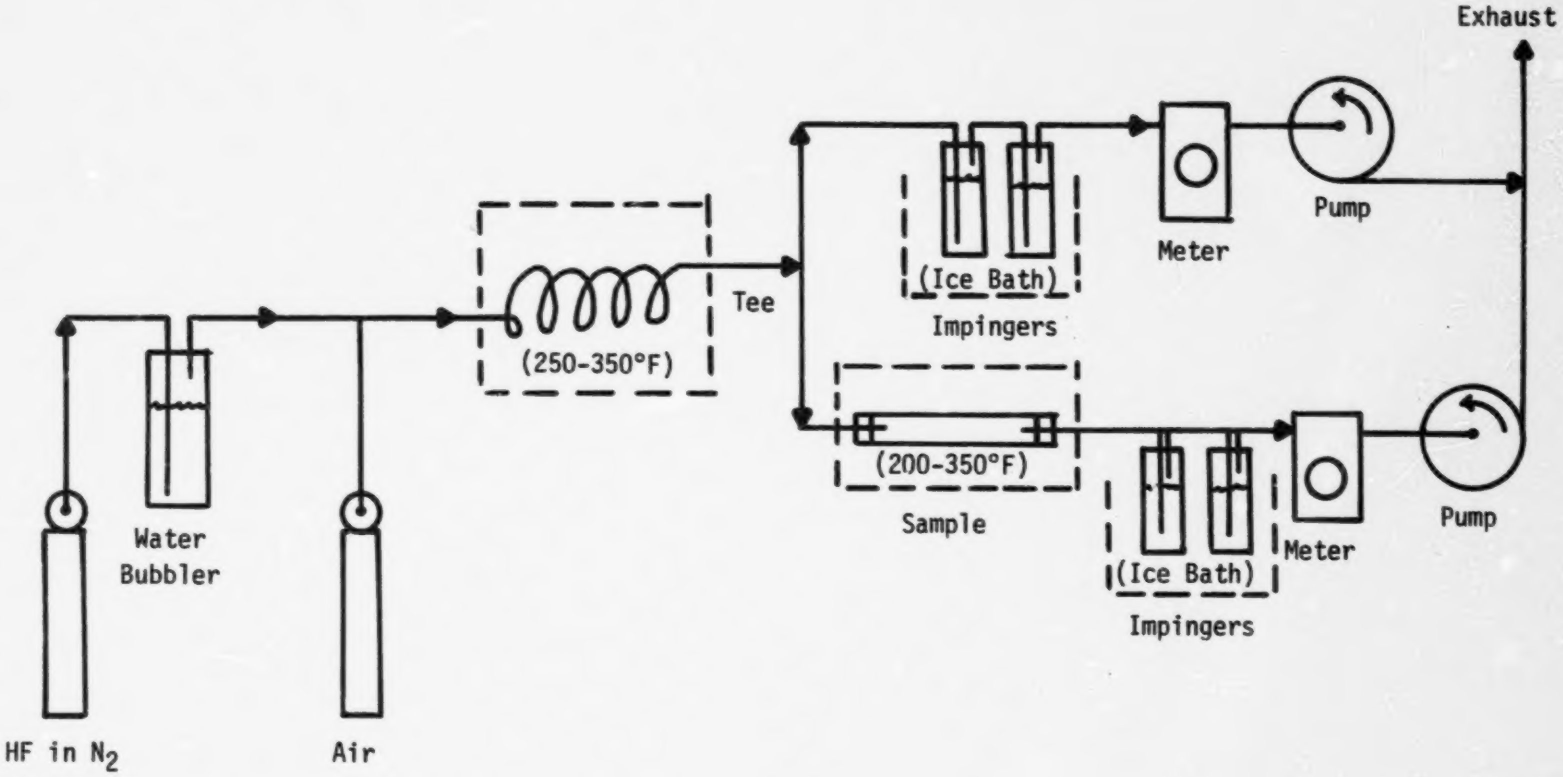
Exhaust
Pump
Meter
(Ice Bath)
Impingers
Tee
(250-350°F)
(200-350°F)
Sample
Pump
Meter
(Ice Bath)
Impingers
Water
Bubbler
HF in N_2
Air

FIGURE 7 SCHEMATIC SKETCH OF APPARATUS FOR EVALUATION OF MATERIALS IN DILUTE HF STREAMS

TABLE 2

INITIAL AND FINAL LEVELS OF FLUORIDE IN AN INERT GAS STREAM PASSING THROUGH HEATED GLASS AND STAINLESS STEEL TUBES

316 STAINLESS STEEL

Run	Time (min)	Tap F^-/ft^3 (moles $X10^{-5}$)	Test F^-/ft^3 (moles $X10^{-5}$)	F^-Test/F^-Tap (X100)
320°F				
A-1	30	0.9	1.0	111
2	30	0.8	1.05	131
3	30	1.25	1.65	132
4	30	1.3	1.6	123
5	40	0.03	0.2	---
6	30	1.15	1.15	100
7	30	1.45	2.0	138
8	30	1.15	1.2	104
9	30	1.3	1.35	104
10	30	0.2	0.2	---
11	180	0.01	0.01	---
12	160	0.00	0.01	---
		Average (8 runs) 1		118
		Standard Deviation		13.7
200°F				
C-13	30	1.2	1.2	100
14	30	1.3	1.2	92
15	30	0.1	0.1	---
D-16	30	1.25	1.0	80
17	30	1.2	1.55	129
18	30	1.25	1.15	92
19	30	1.65	1.4	85
20	30	1.5	1.25	83
21	30	1.4	1.5	107
22	30	0.06	0.13	---
23	30	0.03	0.02	---
24	27	0.02	0.01	---
		Average (8 runs)		96
		Standard Deviation		15.0

BOROSILICATE GLASS

Run	Time (min)	Tap F^-/ft^3 (moles $X10^{-5}$)	Test F^-/ft^3 (moles $X10^{-5}$)	F^-Test/F^-Tap (X100)
320°F				
H-39	30	1.45	1.30	90
40	30	1.45	1.40	97
41	30	1.35	1.35	100
42	30	1.35	1.30	96
43	30	1.35	1.30	96
44	30	1.30	1.25	96
45	30	1.35	1.30	96
46	30	0.05	0.13	--
47	30	0.01	0.04	--
		Average (7 runs)		96
		Standard Deviation		2.6
200°F				
F-29	30	1.55	1.20	77
30	30	1.35	1.30	96
31	30	0.15	0.30	--
32	30	0.02	0.06	--
G-33	30	1.45	1.25	86
34	30	1.40	1.25	89
35	30	1.35	1.35	100
36	30	1.45	1.35	93
37	30	0.09	0.30	--
38	30	0.01	0.09	--
		Average (6 runs)		90
		Standard Deviation		7.3

to be evaluated and then into impingers. The impingers were held in an ice bath and contained 0.1 N NaOH. During the course of a run, the sample tube was maintained at a preselected temperature in the range 200-350°F by means of heating tape to approximate stack sampling conditions. The impinger solutions were subsequently analyzed for fluoride by adjusting pH and carrying out a direct measurement with a specified ion fluoride electrode previously calibrated by standard additions of sodium fluoride.

A series of experiments was carried out with this apparatus at an HF concentration of 10 ppm and sampling rate of 0.1 to 0.2 cfm, utilizing 5-foot lengths of 316 stainless steel and borosilicate glass as samples. Measurement of the volume increase in the impingers showed a 4% water content in the gas stream. Experimental runs generally covered 1 to 4 hours, with collection and analysis of impinger solutions after each 30-minute interval. At the conclusion of a run, the HF stream was turned off and air was allowed to continue to flow through the system. Several additional 15-minute impinger samples were collected to determine the length of time required to purge fluoride from the system.

The experimental data, which is normalized to constant volume, is presented in Table 2. A comparison between the initial (tap off) and final (sample) fluoride concentrations are presented for the stainless steel and glass tubing samples in Figures 8 and 9, respectively. In the case of stainless steel, Figure 8, the observed increase in fluoride after passing through the sample (Run A at 320°F) is attributed to some defluorination of a teflon plug which was used for the gas seal at the front of the stainless tube. With the exception of one bad data point, indicated by an arrow, Run B shows excellent collection efficiency. The 200°F data for stainless steel exhibits considerable scatter, especially in Run D, which is due mostly to experimental adjustments during the course of the run to achieve equal flow rates in the tap off and sample streams. If the six data points are averaged, initial and final stream concentrations agree quite closely; the average of all 200°F data yields a collection ratio of fluoride out to fluoride in of 96% with a stan-

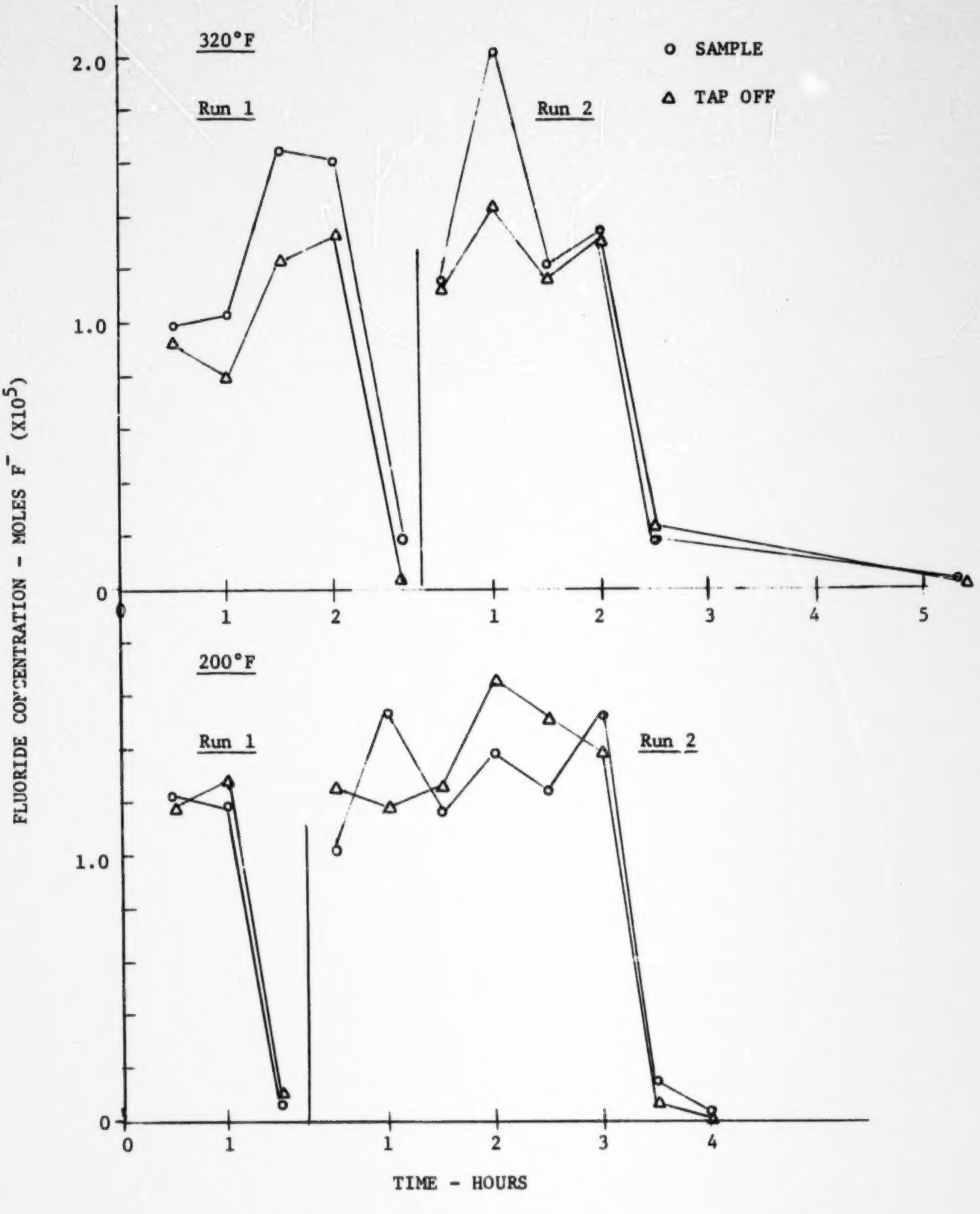

FIGURE 8 A COMPARISON OF INITIAL (TAP OFF) AND FINAL (SAMPLE) FLUORIDE CONCENTRATIONS AFTER PASSAGE THROUGH A FIVE FOOT 316 STAINLESS STEEL TUBE

dard deviation of 15.0. After sampling experiments with the stainless steel were completed, the tube was washed with water. These washings were found to contain 3.1 x 10^{-6} moles of fluoride, indicating very little adsorption of fluoride onto the tube walls.

With the benefit of having determined proper flow rates and other experimental settings from the stainless steel experiments, the data for the glass sample, Table 2 and Figure 9, are considerably more uniform. The outlet concentration was found to be lower than the initial concentration in all samples measured. By averaging the data, the collection ratio for the glass sample is 90% at 200°F and 96% at 320°F, with standard deviation of 7.3 and 2.6, respectively. Probe washings from the glass tube at the conclusion of experiments yielded 1.56 x 10^{-5} moles of fluoride, which is about five times more than what was found in the stainless sample.

The experiments with a 316 stainless steel sample should probably be repeated to reflect the improvements in the experimental procedure that were incorporated in the glass sample experiments. Also, variations in HF concentration and flow rate should be explored. We feel that it is imperative to carry out similar evaluations of collection ratios at levels of HF that more nearly represent well controlled stack (i.e., 0.1 to 1 ppm HF) and flow rates up to 1.5 cfm before a specific probe material for sampling fluorides can be recommended.

2. Sample Storage Since a very significant part of the sample collection procedure involves containment of the collected samples prior to analysis, a laboratory evaluation was carried out to determine the degree to which fluoride ion is lost to the container. For these evaluations, acidic, neutral and basic solutions containing 1 x 10^{-4} molar solutions of fluoride added as NaF and as Na_2SiF_6 were stored in glass and polyethylene bottles for a period of 27 days. During this time, aliquot samples were periodically removed from the containers and their fluoride content measured to ascertian whether or not losses were occuring.

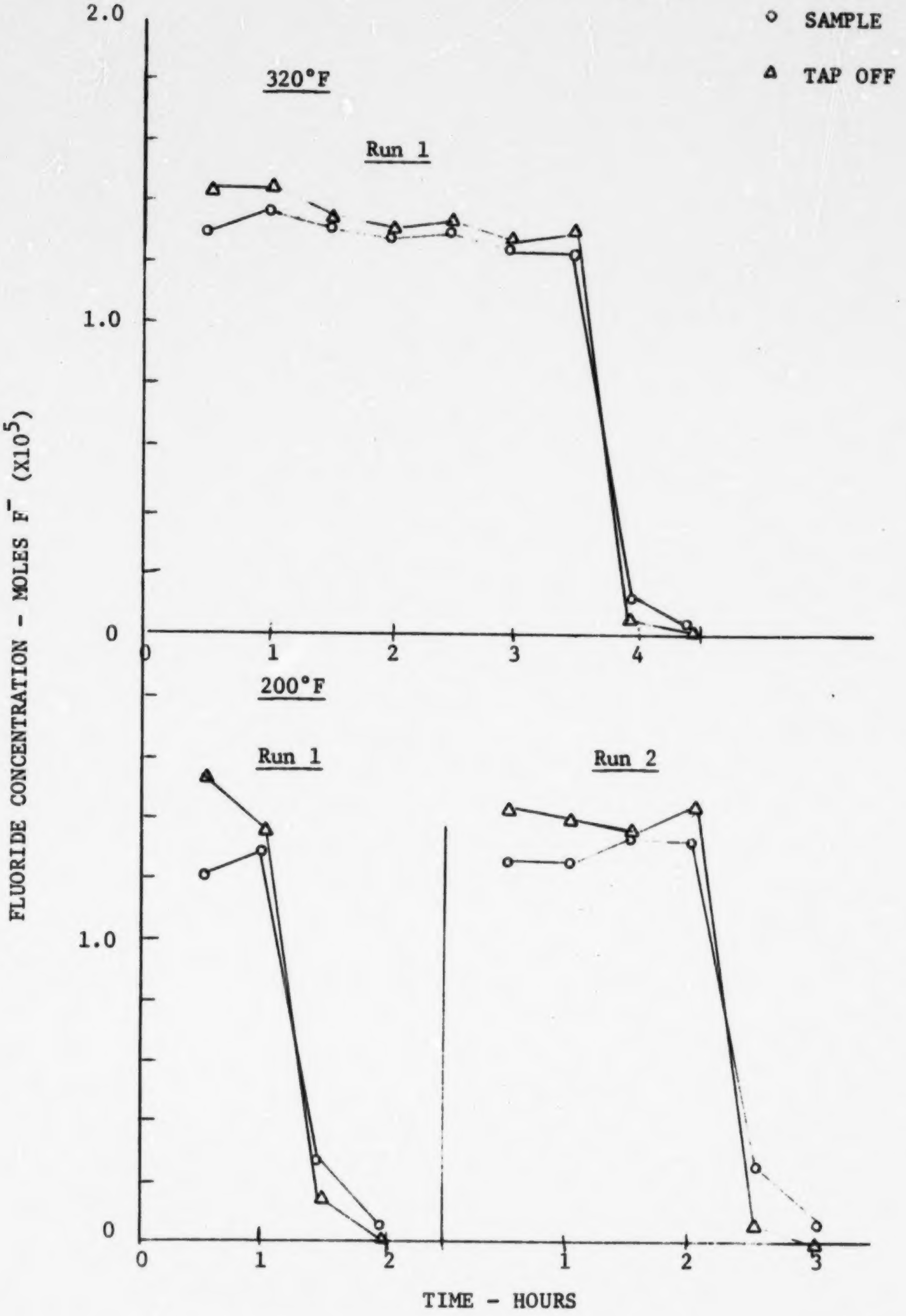

FIGURE 9 A COMPARISON OF INITIAL (TAP OFF) AND FINAL (SAMPLE) FLUORIDE CONCENTRATIONS AFTER PASSAGE THROUGH A FIVE FOOT BOROSILICATE GLASS TUBE

TABLE 3

STABILITY OF DILUTE SODIUM FLUORIDE SOLUTION IN GLASS AND POLYETHYLENE CONTAINERS

Solution	Container Material	Fluoride (moles/liter)*			
		Start	2 Days	7 Days	27 Days
NaF in 0.1N NaOH	glass	9.1×10^{-5}	9.0×10^{-5}	9.9×10^{-5}	10.3×10^{-5}
	polyethylene	0.1	9.4	9.9	$10._1$
NaF in H_2O	glass	$10._1$	9.5	9.8	9.9
	polyethylene	10.1	9.6	9.9	$10._3$
NaF in 0.001N H_2SO_4	glass	9.5	9.0	$10._1$	$10._3$
	polyethylene	9.5	9.1	$10._1$	$10._3$
Na_2SiF_6 in 0.1N NaOH	glass	9.9×10^{-5}	9.4×10^{-5}	9.6×10^{-5}	9.8×10^{-5}
	polyethylene	9.9	9.5	9.8	9.9
Na_2SiF_6 in H_2O	glass	9.8	9.4	9.8	9.6
	polyethylene	9.8	9.6	9.9	9.9
Na_2SiF_6 in 0.001N H_2SO_4	glass	9.3	9.3	9.8	9.9
	polyethylene	9.3	9.4	9.9	9.9

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* Forty (40) ml of sample (pipet) plus 5 ml 1 M sodium citrate were neutralized (citric acid) to bromthymol blue and diluted to 50 ml for measurement by the direct fluoride electrode.

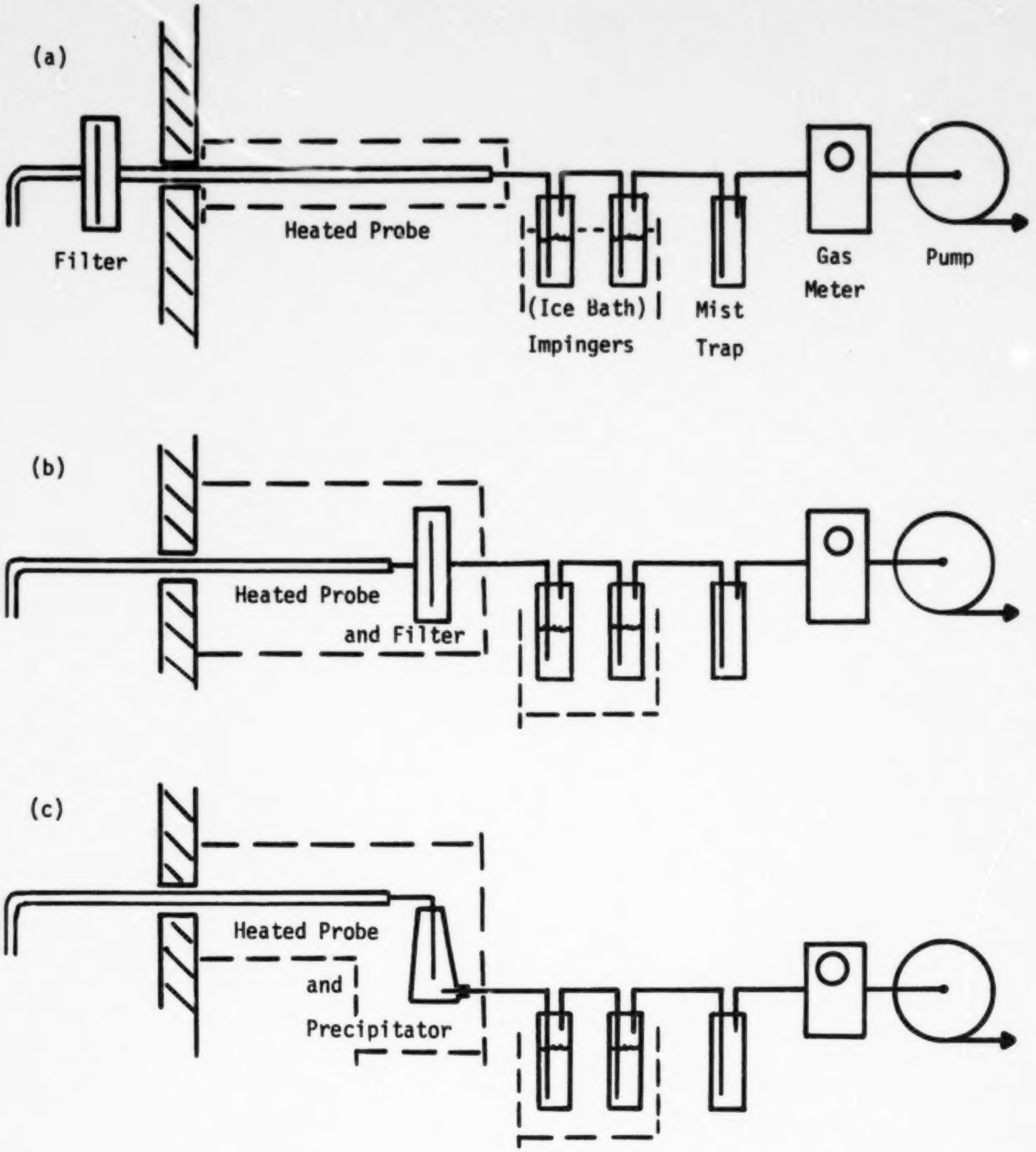

(a)
Filter
Heated Probe
(Ice Bath)
Impingers
Mist
Trap
Gas
Meter
Pump
(b)
Heated Probe
and Filter
(c)
Heated Probe
and
Precipitator

FIGURE 10 SCHEMATIC SKETCH OF FLUORIDE SAMPLING APPARATUS

The glass containers were new flint glass bottles which had been washed with distilled water prior to use. The polyethylene bottles had been used previously, although not for the storage of fluoride solutions and were also washed prior to use. The results of this evaluation are shown in Table 3. In no case is any significant loss of fluoride readily apparent. It is concluded that for these levels of fluoride either flint glass or polyethylene bottles are suitable sample containers. Because of their fragility, however, glass containers are less acceptable for use in the field.

E. Conclusions and Recommendations

Within the four industries considered in this study, primary aluminum, steel and glass manufacturing plants are characterized by "dry" stack gas streams. We would expect that a single sampling train and sampling procedure would be appropriate for all process streams within these industries. A schematic representation of the required sampling train is presented in Figure 10. Particulate and gaseous fluorides would be collected separately. Furthermore, suitable analytical methodology would permit the separation of total fluoride into soluble particulate, insoluble particulate and gaseous fractions. In most cases, the total collected particulate could also be determined with no change in sampling or analysis procedure.

With reference to Figure 10 there are three optional procedures for collecting particulate. In-stack collectors (a) have been used infrequently and there is insufficient background data to support their use at this time. Consequently, the tentatively recommended procedure for particulate collection is either by a filter utilizing either a glass fiber or organic membrane collection media, (b), or an electrostatic precipitator, (c). Any of these would be maintained at temperatures above the water dew point but, in the case of a membrane filter, not in excess of 250°F. Gaseous fluorides would be collected in a series of two Greenburg-Smith impingers containing either distilled water or dilute NaOH.

In difference to these industries, the phosphate rock processing operations are characterized by "wet" emission streams. As a result of copious amounts of water and steam, it is not sensible to attempt a separation of particulate and gaseous fluorides. The same sampling apparatus as shown schematically in Figure 10a could be employed by removing the particulate collection component from the train.

Based upon an examination of the open literature, discussions with industry representatives and our own laboratory evaluations, both 316 stainless steel and borosilicate glass materials are suitable for heated sampling train components, including the probe, precipitator body and filter holder. At lower temperatures (250°F and below), epoxy or plastic-coated metal tubes can be used for the probe. Impingers, mist traps and connectors can be made of glass or polyethylene. The fragility of glass makes it less suitable than the other materials for field sampling.

Sampling should be carried out in a careful manner to provide a high level of reliability. Pre-sampling checkouts should include a velocity traverse, measurement of typical stream water content, etc. In general, sampling should be isokinetic and carried out at one or more points to reflect the "average" stream conditions at a rate of 0.75 to 1.5 cfm. Sampling times should reflect cyclic variations in the process being monitored, but should be at least one hour. All required data should be recorded in an appropriate format to allow subsequent calculations of emission levels and rates.

After sampling, cleanup should be performed carefully to avoid any contamination or loss of sample. Separate containers should be employed for filter (or precipitator) particulate, impinger catch and probe washings. These may be combined during analysis, depending upon analytical requirements. Either glass or polyethylene containers may be used; the latter are recommended due to their ruggedness.

A procedural outline of the tentatively recommended stack sampling procedure is presented in Appendix A. It must be recognized that the alternative components, materials and procedures that are specified must be subjected to field evaluation before final recommendations can be made. Finally, there is presently no basis for determining or estimating the precision, accuracy, sensitivity or detectability of the tentatively recommended sampling methods.

V. SAMPLE ANALYSIS

A. Introduction

Measurement of the fluoride content of solid, liquid and slurry samples collected from various industrial stationary sources requires a combination of analytical techniques including solubilization of the sample, removal of interfering species and fluoride measurement. Numerous methods for accomplishing these procedures have been employed over the years. The most promising approaches, as judged by a critical review of the literature and interviews with several industrial laboratories, have been incorporated into a comprehensive laboratory evaluation of methods, utilizing samples representative of typical emissions from primary aluminum, steelmaking, phosphate rock processing and glass manufacturing industries. From these studies, tentative fluoride analysis procedures have been developed and are recommended as primary candidate methods to be employed in subsequent field test evaluation studies.

This section presents an overview of the requirements of an analytical method; a comprehensive review of existing methodology, including current industrial practice; the results of a laboratory evaluation of candidate methods for sample fusion, distillation and measurement in the presence of various potential interfering chemical species; analysis of several stationary source samples collected in the field to provide insight into the nature of field samples as well as to evaluate the candidate methods; and finally, our conclusions and recommendations.

B. General Considerations

1. Selection of an Analytical Method

Before describing the various methods that are potentially useful for measuring fluoride, the major criteria by which the applicability of a method can be judged are presented. Factors which must be considered include the physical and chemical nature of the samples to be analyzed, the manner in which they were obtained, and the conditions under which the analyses are performed. The chemical nature of the fluoride-containing compounds in conjunction with other compounds which may constitute potential interferences and also the range of fluoride concentrations to be encountered are clearly important. Other factors that should be considered include the simplicity, adaptability, accuracy and precision that is required.

A wide range of fluoride concentrations can be expected for the process effluents encountered in the aluminum, iron and steel, phosphate rock, and glass and ceramic industries. Depending on the particular process and the efficiency of any APC devices employed, fluoride concentrations in the emissions stream can range from less than 0.1 ppm (v/v) to upwards of 50 ppm or more.(1) The amount of fluoride collected during sampling obviously depends on both the sampling flow rate and time; typical practice involves a range on the order of one cfm for a minimum of one hour. For these conditions, the total amount of fluoride collected can range from 0.15 to 75 mg--a dynamic range of 500. Fluoride emissions consist of both particulate and gaseous species; the particulate/gaseous ratio covers a range of 0.1 to 10. In cases where particulate and gaseous fluorides are collected separately and analyzed individually, it is possible that the amount of fluoride in one or the other of the two fractions could be as low as 15 μg. The dynamic range requirement for an analytical method is therefore increased another order of magnitude to about 5,000. The necessity to measure fluorides over such a wide dynamic range with little if any _a priori_ knowledge of the fluoride concentration is clearly a significant constraint on the measurement method.

For the four industries of concern in this study, the chemical nature of the collected sample is widely variable. Chemical compounds that can be expected to be present in the process effluent streams have been given previously in Table 1. Both gaseous and particulate fluoride-containing compounds are emitted from most processes. Hydrogen fluoride and SiF_4 are the most commonly encountered gases. Fortunately, these gases are water soluble and solutions containing them are not particularly difficult to handle analytically. In contrast, particulate fluorides can range from the very insoluble and refractory dryolites and chiolites, to slightly soluble phosphate rock and fluorspar, to very soluble sodium fluoride and sodium fluosilicate. Other species present in the effluent which do not contain fluoride but which can cause potential analytical interferences include gases, such as the sulfur and nitrogen oxides, and solids, having varying solubility in water, containing metals such as aluminum, iron, calcium and silicon.

Another consideration concerns the simplicity of the candidate analytical method. Potential users of the method include personnel associated with federal, state, and municipal regulatory agencies. Since fluorides constitute only one of many pollutants for which laboratory analyses will be required, the candidate method should be sufficiently simple so that a technician who has never previously made fluoride measurements can obtain reliable results in a short time and with a minimum of training and practice.

It is desirable that the method be sufficiently flexible to be easily adapted to future requirements for fluoride measurement. If particular emphasis should eventually be placed on fewer industrial processes than at present, it is possible that the nature of the sample obtained from these processes would be such as to permit a simpler analytical scheme to be used. The present analytical method should therefore be easily modified, preferably by deletion of one or more steps, to meet new requirements.

The accuracy and precision of analytical method is obviously an important factor which must be considered; however, undue emphasis should not be placed on accuracy and precision at the expense of the other considerations mentioned previously. A given analytical method in the hands of a highly experienced analyst may produce results with an accuracy and precision of better than ± 1%. An alternate method may be good to only ± 5-10%, even in the hands of a relatively inexperienced operator having little information on the nature of the sample. This second method may, in fact, be preferable to the more precise method, which in the hands of the inexperienced technician, may produce errors far larger than ± 10%. Additionally, and of more importance, the analytical precision and accuracy must be considered in terms of the magnitude of errors introduced in other steps of the overall measurement. Errors associated with sampling, while not well defined, could be 10-25%, in which case an analytical method precise and accurate to ± 1% is not at all warranted.

The variance (square of the standard deviation) of the overall measurement equals the sum of the variances of the individual measurement steps. Thus, if random sampling errors amount to ± 25%, the use of an analytical procedure good to ± 10% would increase the overall measurement error by only 2%. If random errors in sampling and analysis were both ± 10%, the error in the overall measurement would be 14%. As a base line, it is assumed that an analytical procedure having a precision and accuracy of ± 5-10% is probably sufficient for the measurement of fluorides.

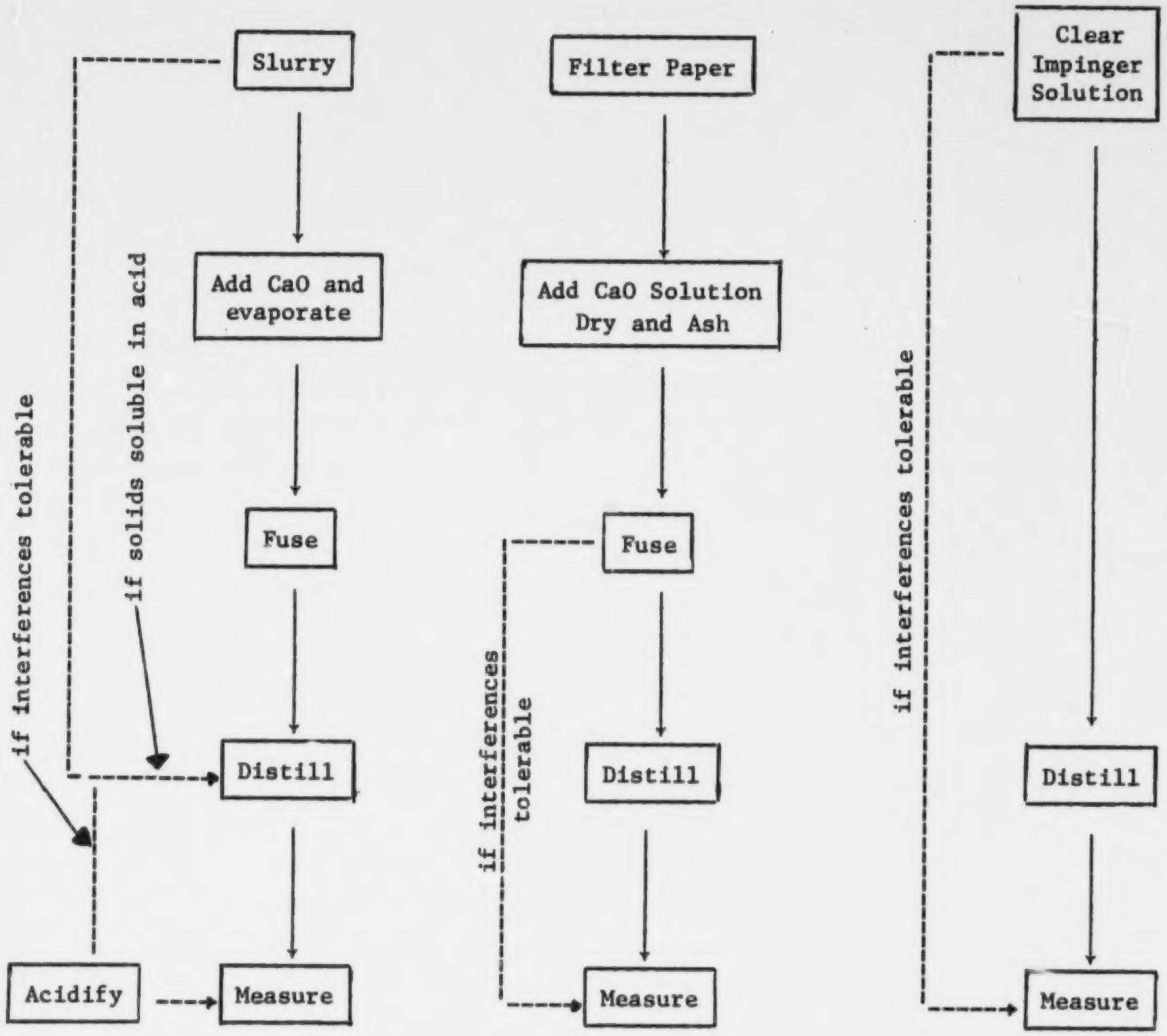
2. Fundamental Steps in Fluoride Analysis Procedures With the exception of certain instrumental techniques, such as X-ray fluorescence and neutron activation analysis, virtually all fluoride analytical procedures involve the measurement of free fluoride ion in solution. In many cases, the actual measurement is the quickest and easiest part of the overall procedure. If the sample to be analyzed contains particulate material, the solids must be put into solution. In cases where there are also other ions in solution which can bind fluoride into complexes, the fluoride must be freed from the complex. Other species present in solution may interfere directly with the chemical reaction or the indicator used in the measurement; such interferences must also be dealt with. Thus, the analysis of fluoride typically involves three steps--dissolution of solids, separation of fluoride from interferences, and finally, measurement of fluoride ion.

Samples obtained from process effluent streams and subsequently returned to the laboratory for analysis can range from clear impinger solutions, containing only dissolved gaseous species, to filter papers containing dry particulate to aqueous slurries containing varying amounts of dissolved and undissolved chemical species. Impingers are normally charged with a total of 200-400 ml of collecting solution. Some condensation occurs during sampling, which increases the final amount of impinger solution. Thus, the gaseous fluorides that are collected are usually presented for analysis in a total volume of 300-500 ml. When the relative humidity of the process stream is very high, as is the case in many streams found in the phosphate rock processing industry, significantly more condensation can occur, and a final impinger catch in excess of one liter is sometimes obtained.

Filter papers containing particulate are usually returned to the laboratory intact; total particulate catch can range from 10-1,000 mg. If a cyclone collector is used ahead of the filter, the filter catch may be only a fraction of the total particulate. If a cyclone is not used, most of the particulate material will be found on the filter paper. In either case, some portion of the particulate usually adheres to the walls of the sampling probe and is collected in the probe washings.

Regardless of the sampling train employed, the sampling probe, cyclone (if used), and filter holder or electrostatic precipitator must be washed to remove all particulate material. The final volume of these washings is again usually on the order of 300-500 ml; in some cases, these washings may contain most of the particulate material collected.

Typical procedures for handling the three types of samples which can be encountered are shown schematically in Figure 11. Because of their widespread use and general applicability, fusion and distillation have been substituted for the more general terms,solubilization and separation, respectively. The normal procedural routes are shown by the solid arrows. In addition, a number of abbreviated procedures are shown by the dashed lines; the condition which must be met for the shortcut to be valid is also given. One common simplification is the elimination of the fusion step if the solids can be brought into solution by other means and if the resulting solution is compatible with the measurement technique being used. This abbreviated procedure is often employed in the phosphate rock industry where the particulate material is usually soluble in acid. A second simplification that is sometimes possible is the elimination of the separation step; this is permissible if the level of interfering species is such



Slurry
Add CaO and evaporate
Fuse
Distill
Measure
Acidify
if interferences tolerable
if solids soluble in acid
Filter Paper
Add CaO Solution Dry and Ash
Fuse
Distill
Measure
if interferences tolerable
Clear Impinger Solution
Distill
Measure
if interferences tolerable

FIGURE 11

Stepwise Procedures for Handling Fluoride Samples

(Slurry can also be filtered and the two fractions treated following procedures for filter paper and clear impinger solutions) that they do not adversely affect the measurement method being used. This simplification may be widely applicable when the fluoride ion electrode is used in conjunction with a complexing buffer to measure fluoride concentrations impinger solutions which contain only dissolved gaseous species.

C. Review of Existing Methodology

Based on a critical review of the literature and on discussions with laboratory personnel in the industries of concern to this study, a number of techniques for sample dissolution, separation of interferences, and measurement of fluoride have been compared to select candidate techniques for further testing in the laboratory. Means for effecting each of the three principle analytical steps are discussed in the sub-sections which follow. In addition, a discussion of techniques which are being used successfully in the laboratories of the industries of concern is also included.

1. Measurement Procedures Candidate procedures for measuring fluoride which can be considered candidates primarily involve volumetric or colorimetric determinations or the use of the fluoride specific ion electrode. A variety of other techniques have been used for measuring fluoride in specific cases. Many of these are of limited general applicability and/or require complex, expensive instrumentation. For these reasons, these other techniques are not considered to be candidates for use in a widely applicable standard method, and they will not be discussed further. For a rather complete discussion of such techniques along with references to the original literature, the reader is referred to the recent RRI/TRW report.(1)

a. Volumetric Techniques

Fluoride ion can be determined volumetrically by titrating with salts of one of a number of metals such as thorium, zirconium, iron, aluminum, or lanthanum, all of which form stable fluoride complexes in solution. The most commonly used titrants are the thorium and lanthanum nitrates.

The titration endpoint is usually determined from the color change of an indicator dye such as Alizarin Red-S, Purpurin Sulfonate, or Eriochrome Cyanine R.(11) The indicator color change at the endpoint is either observed visually or measured photometrically; the latter procedure is more time consuming but eliminates the human judgmental errors that are often associated with a visual observation of the faint color change at the endpoint.(12,13) Non-colorimetric means of endpoint detection have been used. They include the fluoride ion electrode,(14) fluorescing indicators,(15) oscillometry,(16) and conductometry.(17)

Of the many reported schemes for volumetric fluoride analysis, the most widely accepted and employed is still the titration with thorium nitrate using Alizarin Red-S indicator. This method is described in detail in the ASTM Method for Inorganic Fluoride in the Atmosphere (D 1606-60). Its advantages and limitations are generally similar to most volumetric fluoride methods. It can be used for a wide range of fluoride concentrations--0.005-10 mg--a 2,000-fold range. However, variations in the procedure are recommended for making measurements of fluoride concentration in the range of 0.005-0.01 mg, 0.01-0.05 mg, and 0.05-10 mg. Thus, to use the method over its widest possible dynamic range, some knowledge of the approximate fluoride concentration must be available--either from prior experience or from trial and error determinations on separate aliquots of the same sample.

If the solution to be titrated is carefully freed of interferences and the method is put in the hands of an experienced technician, the thorium nitrate titration is one of the most accurate and precise fluoride measurement techniques, particularly in the upper part of its applicable concentration range. Precision and accuracy of better than ±1% can be obtained.

The method suffers from a variety of interferences; a careful distillation from perchloric acid is almost always required to provide an interference-free solution for titration. Ions such as phosphate, sulfate, and oxalates interfere in the titration by forming precipitates or complexes. Nitrates, peroxides, sulfides, and sulfites interfere with the formation of the indicator color. Aluminum and silicon interfere by inhibiting the release of fluoride during the distillation. In the presence of significant amounts of these metals, a double distillation, first from sulfuric acid and then from perchloric acid, is often required.

One of the primary reasons for choosing a volumetric determination, the fact that there is usually a known constant stoichiometry of reaction between the sample and titrant, is often not true for titrations of fluoride, particularly at low fluoride concentrations. Consequently, the use of a calibration curve generated by titrating known amounts of sodium fluoride is generally required. Finally, the method requires a high degree of manipulative technique. The titration is usually performed with a microburet to minimize sample dilution by the titrant; reproducible detection of the indicator color at the endpoint requires a good deal of practice on the part of the analyst.

b. Colorimetric Techniques

Most of the colorimetric techniques utilized for the determination of fluoride involve the bleaching by fluoride ion of a colored metal-indicator complex. A few of the better known methods of this type include aluminum-Eriochrome cyanine R,(18) thorium-thoron,(19) zirconium-Alizarin Red-S,(20) and zirconium-SPADNS.(21,22) Methods of this type which involve the bleaching of a color have the disadvantage that the initial solution is highly colored. Low concentrations of fluoride reduce the color intensity only slightly; thus the analysis requires that a small difference between two large absorbence readings be measured accurately.

Recently, a number of direct color reactions, in which the color intensity is directly proportional to fluoride concentration, have been reported. These include use of the chloranilate salts of lanthanum(23) and thorium;(24) fluoride forms a complex with the metal ion releasing highly colored free chloranilic acid. Fluoride reacts with Lanthanum-Alizarin complexone reagent to form a single complex species which is intensely blue in color.(25)

Colorimetric methods in general are more sensitive than volumetric methods and can be used with a smaller sample as well. Precision and accuracy are generally about ± 5%. Many of the methods can detect as little as 0.01 μg/ml of fluoride. Virtually all methods require that a calibration curve be generated from known standard fluoride solutions. Using a given reagent system, the calibration curve is usually linear over a ten- or twenty-fold concentration range. To extend the range of concentration to which a method can be applied, the sample can be diluted or a different reagent system must be chosen. It is possible, by selecting appropriate reagents, to measure fluoride concentrations ranging from 0.2 mg/ml (Iron-Ferron reagent, range 0.01-0.2 mg/ml) to 0.01 μg/ml (Lanthanum-Alizarin Complexone reagent, range 0.01-0.4 μg/ml.)(8) In any event, the use of colorimetric techniques over a wide dynamic range requires some prior knowledge of the approximate fluoride concentration.

Similar to the volumetric methods, colorimetric fluoride methods are subject to a variety of interferences; many of them the same species interfere for the same reasons. Typical interferences include aluminum, iron, phosphate, sulfate, chloride, oxalate, and nitrate. Reliable colorimetric methods, therefore, usually require a prior separation of fluoride from interferences by distillation or diffusion.

c. The Fluoride Specific Ion Electrode

In 1966, Frant and Ross(26) reported the development of an electrode containing a membrane fabricated from a single crystal of lanthanum fluoride which had been doped with divalent europium. The electrode was capable of selectively measuring fluoride activity in solution over a wide range of fluoride concentrations. Since that time the electrode has received a great deal of attention and has been evaluated in many laboratories on a wide variety of fluoride-containing samples.

Of all the measurement techniques for fluoride, the fluoride electrode is the least sensitive to interfering species and has the widest dynamic range. It is useable (and a linear calibration curve can be obtained) for fluoride concentrations ranging from 10^{-1} to 10^{-6} M (2,000-0.02 μg/ml).(27)

Measurements can be made routinely in as little as one milliliter of solution,(28) and on even smaller volumes if the electrode is modified slightly.(29)

The only known interference in the electrode reaction is due to hydroxyl ion; the electrode response to hydroxyl ion is the same as its response to fluoride. Thus at high pH, small variations in pH can introduce sizable errors into the measurement of low concentrations of fluoride. However, if pH is held in the region of 5-7, pH variations have no effect even at the limit of detection of the electrode.

Like all analytical techniques employing an electrode reaction, the fluoride electrode response is proportional to activity rather than to concentration. However, valid concentration measurements can be made if care is taken to be sure that the fluoride ion activity coefficient is the same in calibration and unknown solutions. Changes in activity coefficient are usually caused by variations in the ionic strength of the unknown solution. These effects can be eliminated by adding to the unknown solution a volume of high ionic strength buffer (often 2 M) to swamp out small differences in ionic strength of dilute solutions. Frant and Ross(30) have coined the acronym TISAB (total ionic strength adjustment buffer) to describe a family of buffers of this type. Sodium chloride is usually used to achieve the described high ionic strength. Sodium acetate/acetic acid is sometimes included to provide pH buffering.

Like the volumetric and colorimetric techniques discussed previously, interference in the fluoride electrode measurement can be caused by the presence of species in the sample which complex fluoride ions; the electrode only measures the activity of free fluoride ion. If cations such as aluminum, iron, or calcium are present at a very high level, a separation step may be necessary. However, at moderate levels, the effect of these interferences can be removed by adding a complexant to tie up the metal and release the fluoride. Edmond(31) and Tusl(32) both report good success by adding 0.5 M citrate to complex calcium ion in measurements of phosphate rock samples. Oliver and Clayton(33) used IM citrate to minimize the interference due to aluminum that was present in a variety of samples. Unfortunately, citrate also tends to react with the lanthanum in the electrode membrane and causes the electrode membrane and causes the electrode response to become increasingly slow at low fluoride levels (less than 10^{-4} M). Ingram(34) has found that the use of nitrate along with the citrate is beneficial in minimizing the deleterious effects of citrate on the electrode.

With the exception of hydroxide, ionic strength, and certain cations, the fluoride electrode is virtually interference free. Notably absent are interferences due to anions such as sulfate, nitrate, phosphate, and chloride which plague many other methods. The precision and accuracy of fluoride electrode measurements has been reported by many workers and generally is in the range of from 1-5%. This range of precision and accuracy probably reflects in large measure the varying amount of care with which the measurements were made. The temperature of the sample solution will change the electrode response; a change of 1°C will produce a 1.5% relative error in the measurement.(33) Lack of stability and/or resolution in the pH meter or electrometer used to measure EMF can introduce significant error. An error of 1 millivolt in the EMF measurement produces a relative error of 4% regardless of the absolute concentration being measured. Failure to adequately deal with the problem of slow electrode equilibration particularly at low fluoride concentrations can also lead to significant errors.(34)

2. Solubilization Techniques

a. Fusion

The most generally applicable technique for putting unknown insoluble materials into solution is to perform a fusion with an alkaline flux. In the case of fluoride, the insoluble material is converted to the alkali metal fluoride, which, upon subsequent dissolution of the melt, is water soluble. General procedures for handling particulates on filter papers or in slurries are described in the ASTM Standard Method for

Inorganic Fluoride in the Atmosphere (D 1606-60). Filters must be ashed prior to fusion to destroy the paper and any other organic materials that are present. Ashing at a temperature less than 600°C until no carbon remains is of vital importance. If carbon is present during the fusion, fluoride losses can occur. The filter paper is first wetted with low-fluoride lime water to prevent loss of volatile fluorides, and the ashing is then performed at 550-600°C. The solids remaining after ashing are mixed with a quantity of the flux and fused over a burner or in an electric furnace. Because of the corrosive nature of the fusion, it is usually carried out in nickel, platinum, or Inconel crucibles.

Slurries can be treated in one of two ways. The slurry can be filtered and the filter paper treated as described above. After fusion, the solids can be redissolved in the filtrate fraction. Alternatively, separate analyses of the fused solids and filtrate can be performed. A second procedure is to evaporate the total slurry to dryness, add flux, and perform the fusion. Low-fluoride calcium oxide must be added prior to evaporation to minimize evolution of volatile fluorides as the evaporation proceeds. The choice between filtering or evaporating a slurry is not well defined. The filtration procedure is probably more time consuming in that an ashing and perhaps two fluoride measurements are required, but filtration does eliminate the possible fluoride losses to the atmosphere and to the sides of the vessel that can occur during the evaporations step.

The choice of a fusion flux is somewhat arbitrary; sodium hydroxide and sodium carbonate are the most widely used. The ASTM Method D 1606-60 recommends a fusion with sodium hydroxide; VanLoon(35) has reported successful fusions of cryolite and chiolite with this flux. Farrah(8) and Oliver and Clayton(33) have used sodium carbonate to fuse a variety of samples encountered in the aluminum industry. The latter workers also used a mixture of sodium carbonate and sodium borate to more completely solubilize particularly intractable materials. Evans and Sergeant(36) and Guth and Wey(37) both have reported the use of sodium carbonate fusions in conjunction with the analysis of fluorides in rocks and minerals.

b. Acid Dissolution

For materials known to be acid soluble, the fusion can be replaced with a simple dissolution in acid. This approach is widely used in the analyses of phosphate rock and related materials.(31,32,38,39) Care must be taken to minimize losses of volatilized fluorides from the acidic solutions. Acid dissolution followed by a direct electrode measurement of fluoride in the resulting solution is often feasible. If an acid distillation must be performed prior to measurement, the solid material can be introduced directly into the distillation flask.

c. Pyrohydrolysis

A pyrohydrolytic technique which, in essence, combines the steps of solubilization and separation into one has been reported by Clement, et al.(40) They report that the procedure is particularly effective in removing fluoride from intractable rock and mineral samples. The sample is mixed with a flux composed of bismuth trioxide, sodium tungstate, and vanadium pentoxide. The mixture is then heated at 700-750°C in the presence of a flowing stream of water vapor. Fluoride is evolved from the sample as HF and is collected in alkaline solution for subsequent measurement.

d. Ion Exchange

Cation exchange resins have been used to effect the dissolution of phosphate rock samples.(39) About 5 grams of resin in the acid form is agitated with a 50-ml water slurry of the sample to be dissolved. The cation exchanger binds calcium, and the fluoride anions go into solution. A period of shaking of up to four hours may be required for complete dissolution, after which the mixture is slurried into buret tube and rinsed with a few column volumes of water to flush out all fluoride. The resulting solution is then diluted to volume for subsequent analysis.

3. Removal of Interfering Species The need for and choice of a technique for removal of potentially interfering species depends both on the nature of the sample to be analyzed and the characteristics of the measurement method which is to be employed. The better known techniques include distillation, diffusion, and ion exchange; these three techniques are discussed separately in subsequent sections. The removal of the effects of interfering cations by masking with ligands that complex the cation has been discussed previously in connection with the fluoride ion electrode measurement technique.

a. Distillation

The steam distillation of fluoride as fluosilicic acid from strong acid solution is one of the most widely employed separation techniques. Its use for purifying fluoride samples prior to volumetric measurement was reported by Willard and Winter in 1933.(41) Their procedure, which is still widely employed, involves a distillation from perchloric acid at 135°C. Steam is introduced into the heated distilling flask to help strip out fluoride and to keep the pot volume and temperature constant throughout the distillation. Later variations of this basic approach include the use of other acids such as sulfuric(42) and phosphoric(43) as well as the drop-wise addition of water in place of the introduction of steam.(44) Despite the variations, all of the distillations are carried out at a constant, relatively low temperature so that the carry-over of volatile materials which could interfere in subsequent volumetric or colorimetric measurement is minimized.

In the presence of large amounts of materials such as aluminum and silicon which form soluble fluoride complexes in solution, the vapor pressure of fluoride is markedly reduced and a long distillation time is required for complete fluoride evolution. Since the vapor pressure increases with temperature, a double distillation is usually employed when large amounts of these interferences are present. The sample is first distilled from sulfuric acid at 165°C to isolate the fluoride from the aluminum. The sulfuric distillate is then redistilled from perchloric acid at 135°C to separate the fluoride from the traces of sulfuric acid and other volatile materials that had been carried over during the sulfuric acid distillation.

Despite the tedium of the constant temperature distillation, the basic Willard-Winter approach is still widely used and has become a standard of comparison by which other separation techniques are judged. It is specified in the ASTM Method for Inorganic Fluoride in the Atmosphere (D 1606-60). The distillation can be applied to widely ranging amounts of fluoride in a sample. The distillation as described in the ASTM method can handle samples containing 0.005-10 mg fluoride in a solution volume of 50 ml or less. Cross contamination from high fluoride samples to low ones is a distinct problem, and separate stills are usually reserved for samples containing very small amounts of fluoride. A second reason for the continued use of the Willard-Winter distillation is due to the fact that titration with thorium nitrate continues to be a "reference" measurement method. That titration demands an interference-free solution that generally requires a distillation from perchloric acid.

In an attempt to develop a simpler approach to distillation, Bellack(45) studied the distillation of fluoride from sulfuric acid and concluded that a direct distillation without addition of either water or steam could work effectively and required a great deal less operator attention. The procedure involves the use of a 1-liter distillation pot which is first charged with a mixture of 200 ml concentrated sulfuric acid and 400 ml of water. The acid solution is then distilled until the pot temperature reaches exactly 180°C. The collected distillate is discarded. This "pre-distillation" serves to adjust the acid/water ratio in the pot and also to strip out traces of fluoride that are normally found in the sulfuric acid. After the distillation pot has cooled, the sample in 300 ml of solution is introduced into the pot and distillation of the sample is carried out until the pot temperature again reaches 180°C.

The acid in the distillation pot can be reused for subsequent samples until the metal ion concentration becomes so high that the evolution of fluoride is retarded. The ASTM procedure for Determining Fluoride Ion in Industrial Water and Industrial Waste Water (D 11179-68) incorporates what is essentially Bellack's method. The maximum and minimum amounts of fluoride that can be distilled using this procedure have not, to our knowledge, been fully explored. In his original work, Bellack(45) obtained good recoveries using 300 ml samples containing fluoride concentrations ranging from 0.09-10.0 mg/ℓ. At fluoride concentrations in excess of about 3 mg/ℓ, a small amount of fluoride has been found to remain in the condenser at the end of the distillation. When this is the case, it is recommended that the condenser be disconnected and flushed with 300-400 ml of water, and the washings added to the distillate prior to measurement. This distillation procedure can be used only if appropriate measurement techniques which can tolerate a small amount of sulfate carry-over near the end of the distillation are employed. Bellack(45) successfully used the Zirconium-SPADNS colorimetric method on distillates obtained by the direct distillation procedure.

b. Diffusion

Diffusion of fluoride from an acid solution to an alkaline solution or solid alkaline absorbent at temperatures well below the boiling point of the acid solution is a well established procedure. It has been utilized primarily as a technique for separating microgram and sub-microgram amounts of fluoride from very small samples in biochemically oriented research.(28,46,47) The technique is based on the early developments of Conway;(48) the acid solution containing the fluoride sample is placed in one compartment of the diffusion cell and the alkaline receiving medium is placed in a second compartment. The cell is then sealed and diffusion is allowed to proceed. After diffusion is complete, the cell is opened and the alkaline receiving medium is subjected to one of a variety of fluoride measurement techniques.

The diffusion is usually performed at temperatures ranging from 25-60°C. Over this temperature range, the fluoride vapor pressure is very low, but this effect is counteracted by placing the alkaline and acidic solutions in close proximity and employing diffusion times of up to 24 hours or more. It has been reported that the addition of siloxane derivatives can markedly speed the diffusion process; diffusion times at 25°C of under 6 hours have been reported.(49) Tusl(50) found that silicone grease had a similar accelerating effect.

The technique of diffusion can produce good fluoride separations, but it has not been used extensively for the types of samples expected from process effluent streams. Of major concern is the effect of sizable amounts of aluminum or iron on the vapor pressure and consequently the diffusion rate of fluoride.

c. Ion Exchange

A variety of procedures for separating fluoride from cationic and/or anionic interferences by the use of ion exchange have been reported. Anion exchange resins in the dydroxide or acetate form have been most widely employed. Fluoride can be trapped on Amberlite IRA-400 and subsequently eluted with 10% sodium chloride solution.(51) Ziphin, et al(52) have performed a gradient elution with sodium hydroxide to separate fluoride from phosphate. The separation of fluoride from iron, aluminum, phosphate, and sulfate by stepwise elution from an ion exchanger with sodium acetate has also been reported.(53)

While ion exchange has been used successfully and is an attractively simple separation approach, it should be used cautiously on ill-characterized field samples. The separation itself depends upon the formation of a resin-fluoride complex. The presence of unexpected interferences in solution which could also form fluoride complexes could change the fluoride distribution coefficient between the stationary and mobile phases and lead to unexpected erroneous results.

4. Current Industrial Practice Analytical methods for fluorides that are currently being used in the aluminum, iron and steel, glass and ceramic, and phosphate rock industries were surveyed by means of personal communication with analytical chemists and environmental control engineers at selected companies within each industry. With very few exceptions, the same general methodology and practice is found in all four industries, so a single comprehensive discussion of our findings will be presented. Analytical methods presently in use vary to some extent from company to company and even between the various plant locations of a single company.

In general, the Willard-Winter perchloric acid distillation followed by titration with thorium nitrate is the "accepted" procedure and alternate methods are evaluated by comparison to it. With regard to the acceptability of newer techniques such as the fluoride specific ion electrode and various colorimetric methods, one encounters opinions ranging from outright rejection to acceptance as valid. The tendency to reject the newer, simpler methods seems to be related somewhat more to the sense of achievement that a given analyst experiences when he does a good thorium nitrate titration than it is to the results of comparative collaborative tests. For many industrial laboratories, fluoride analysis for emission control purposes is relatively new and represents only a small portion of the overall analytical load. These laboratories were previously performing fluoride analyses for the purposes of process control or product specification many years ago when the thorium titration was the only available reliable technique. Consequently the titrimetric method was written into a great many process control and customer acceptance analysis procedures, and once so written, there is a great deal of inertia which prevents change.

For industries and processes where particulates are collected as a separate fraction, the normal procedure involves ashing the filter paper, fusing the solids, distilling from perchloric acid, and finally titrating with thorium nitrate. One exception is the phosphate rock industry, where solids are acid soluble and the fusion step is unnecessary. Sodium hydroxide seems to be the preferred flux for fusing samples.

Perchloric acid in the distillation is retained because of its low contribution to the reagent blank and also because a final distillation from perchloric acid at 135°C is necessary for a successful thorium titration. Although the constant-temperature Willard-Winter distillation can be tedious when performed only occasionally be an inexperienced technician, it becomes more or less routine when the same technician performs a sizable number every day. Operating conditions become optimized to the point where the distillation flask is charged, set on the heater, the steam line is connected, and the distillation proceeds virtually unattended at the correct temperature. Similar considerations apply to the thorium nitrate/Alizarin Red-S titration with its "hard to see" endpoint. After much experience with the technique, the faint color change is easily perceived. In one laboratory, for example, a certain single analyst does all of the "important" thorium nitrate titrations; he has been doing so for nearly 20 years. In one laboratory visited, the Zirconium-SPADNS colorimetric method has been used to analyze modified Willard-Winter distillates for some time and has been found to be completely satisfactory. We encountered no one who was using the fluoride specific electrode to measure distillates.

One major company has found the Technicon Auto-Analyzer procedure(54) to be an ideal compromise between speed, simplicity, and accuracy. In the Technicon procedure, a continuous micro-distillation from sulfuric acid is performed and the distillate is measured colorimetrically with the Lanthanum-Alizarin complex one reagent. A second laboratory tried the technique and discontinued it; because their sample load was rather low, the ratio of analyses performed to required maintenance time was poor. Since the technique has a limited dynamic range, they found that it was frequently necessary to rerun samples using a new aliquot size when analyses were being performed on samples having unknown fluoride concentrations. It was suggested that a fluoride ion electrode measurement in conjunction with the Auto-Analyzer might result in an automated method with better dynamic range.

The direct fluoride ion electrode measurement after buffering seems to be generally accepted and is employed for measuring fluoride in impinger solutions collected after a particulate filter. In the phosphate rock industry, where wet streams demand that gases and particulates be collected together in an impinger, direct electrode measurements are made in the slurry after buffering. Initially, all process effluent samples collected by one company were run by both this technique and the conventional Willard-Winter distillation/thorium titration. Reasonable agreement between results was found, and now only an occasional sample is distilled as a check and in the event that elevated levels of fluoride are found in the effluent. In that case, the sample is submitted for a confirmatory analysis by distillation and titration.

Attention to "good analytical practice" is necessary for reliable fluoride measurements, especially at low concentrations. Collaborative testing using real samples is done continually within given industries. This procedure serves as a quality control check on the ability of a given laboratory to run "the accepted method," and also provides a means for evaluating and comparing potentially useful new methods.

It is very important to exercise caution to avoid external and cross contamination of samples. Some laboratories distill their own water and filter the laboratory air through charcoal and lime. Seemingly innocuous occurrences such as the use of a holocarbon-charged aerosol can in the laboratory can result in sample contamination. The use of completely separate distillation flasks and muffle furnaces for samples of high and low concentrations is strongly suggested. Finally, it is absolutely necessary that alkaline conditions be maintained when flouride-containing samples are ashed or evaporated so that there is no fluoride loss through volatilization.

5. Comparison and Summary of Candidate Techniques

a. Measurement Procedures

Of the available fluoride measurement techniques, the fluoride electrode appears to be the clear choice by virtually all criteria. Its wide dynamic range of about 10^{-5}, as compared to a maximum of about 100 for colorimetric techniques and 200 for volumetric (titrimetric) techniques, makes it well suited for measuring the wide range of fluoride concentrations which can be encountered. Titrimetric procedures can produce the best precision and accuracy; at the higher fluoride levels within the range to which titrimetry can be applied, precision and accuracy of better than ± 1% is possible, but can become ± 5% or more when performed by an unskilled analyst. In comparison, colorimetric and specific ion electrode measurements are typically good to about ± 2-5% when performed by a relatively unskilled technician. In any event, if one considers the magnitude of other errors which could be encountered in the overall sampling and analysis procedure, a precision and accuracy of better than ± 2-5% in the measurement step is probably not warranted.

Because of its freedom from anionic interferences, the fluoride ion electrode is particularly well suited to the direct measurement of gaseous fluorides collected in impingers. Interferences in colorimetric and volumetric procedures resulting from oxides of sulfur and nitrogen as well as other gases which are frequently encountered in emission samples generally require a separation step prior to measurement. Interferences due to cations usually manifest themselves by complexing fluoride in the sample solution being measured, and consequently, affect all measurement techniques in more or less the same way.

There is very little difference in the actual time required to perform a measurement by either of the three types of techniques. Both the colorimetric and electrode methods are equally simple to perform and require little operator skill. On the other hand, the titration definitely requires a dedicated and skilled technician. While the visual titrimetric procedure requires less expensive laboratory apparatus, this factor alone cannot make up for its limitations.

b. Solubilization

Fusion in sodium hydroxide or sodium carbonate seems to be the only reliable way to handle a variety of unknown particulate materials. Pyrohydrolysis would probably work as well, but the technique seems needlessly complex. However, if pyrohydrolysis were to be run more or less continuously on a high volume of samples, it would probably be faster than the equivalent fusion/distillation combination. Other means of dissolving samples exist, but they are not as universally applicable to ill-characterized materials as is the alkaline fusion technique.

c. Separation of Fluoride

Removal of interfering species by distillation appears to be the method of choice. While ion exchange techniques are simple, the possibility exists that unexpected species in solution might disturb the sorbtion behavior of fluoride ion; incomplete separation and/or non-quantitative recovery could result. The choice between distillation and diffusion is less clear. The fundamental principles involved are so similar that both should work. However, there has been very little experience with diffusion separations of samples of the type expected in this application--relatively large volumes of solution containing significant amounts of aluminum and iron.

There is no evidence that sulfuric acid is any less capable of producing quantitative fluoride recoveries than any of the other acids commonly used. In fact, with perchloric acid at 135°C, the reverse is sometimes true. When significant amounts of aluminum are present in the sample, a pre-distillation from sulfuric acid must be performed prior to the perchloric acid distillation. On the assumption that the fluoride specific ion electrode, with its freedom from sulfate interference, is used for the measurement step, a single distillation from sulfuric acid should suffice. The fact that the fluoride electrode is generally free from anionic interferences (most of the volatile interference that distill over hydrolyze to anions) should also relax the restriction on precise control of distillation temperatures; this, in turn, should result in less operator effort if not in overall distillation time.

We believe that the base separation method is a distillation from sulfuric acid. This could take the form of a direct distillation similar to the one described in ASTM Method D1179-68, or it could be a distillation with steam or drop-wise water addition with only minimal temperature control. The relative merits of the two approaches have been compared and will be discussed in the section on laboratory studies which follows.

D. Laboratory Evaluation of Candidate Techniques

1. Evaluations of the Fluoride Specific Ion Electrode as a Measurement Technique

Studies were preformed to evaluate the effect of interfering species such as iron and aluminum on the fluoride electrode measurement. Its performance was compared with the zirconium-SPADNS colorimetric method using a set of simulated field samples. In addition, a set of actual phosphate rock industry samples were analyzed in two different laboratories using the fluoride electrode to assess its performance in a practical situation.

a. Apparatus and Procedure Fluoride measurements were made with an Orion fluoride electrode (Model 94-09) used in conjunction with silver/silver chloride, 4M potassium chloride reference electrode. In the initial phase of our study, the EMF between the fluoride electrode and the reference electrode was measured with a Beckman Expandomatic pH meter. Later in the program we switched to an Orion Model 800 digital pH meter for all succeeding measurements.

Fluoride standards were prepared by diluting Orion standard fluroide (0.1M) solution. A calibration curve was prepared by plotting EMF as a function of logarithm of concentration using seven known solutions spanning the concentration range from 10^{-2} - 10^{-6} moles/liter fluoride.

Measurements of unknowns were performed by reading the electrode EMF and converting to concentration by referring to the calibration curve.

When measuring fluoride concentrations less than 10^{-4} M, a slight drift on the order of 1-2 millivolts was observed during the first few minutes after immersing the electrode. When working at these levels, measurements were made at a fixed time interval of five minutes after immersion to minimize the effect of drift.

The electrode measurement was performed on a final solution volume of 50 ml. A 25 ml sample of the solution to be measured was taken, bromthymol blue indicator was added, and the pH adjusted, if necessary, to be within the range of 6.6-7.1, the range where the indicator is green in color. Sodium citrate solution was then added (10 ml of 2.5 M or 5 ml of 1.0 M for final citrate concentrations of 0.5 M and 0.1 M, respectively), and the resulting solution diluted to 50 ml.

Measurements using the zirconium-SPADNS method followed the procedures described in ASTM Method D1179-68. Details of the distillation procedures are found in Part 3 of this Section.

b. Results and Discussion

1) Effect of Interfering Species To evaluate the potential use of the fluoride specific ion electrode the direct measurement of fluoride-containing solutions without prior separation of interferences, a relatively high level of sodium citrate (0.5 M) was utilized. In addition to complexing interfering cations, this high concentration of sodium citrate tends to produce a solution of essentially constant ionic strength by swamping out the effects of small differences in salt content of the unknown sample.

Two of the most important interfering cations for the industries of concern are aluminum and iron. Measurement of known concentrations of fluoride in solutions containing varying excesses of aluminum are shown in Table 3A. Accurate measurement is clearly related to both the concentration of aluminum (more precisely the aluminum/citrate ratio) and the

Table 3A

Effect of Aluminum (III) on Fluoride Electrode Measurement in 0.5 Molar Citrate Buffer

Fluoride Added$^{(a,b)}$	Aluminum Added$^{(a,c)}$	Mole Ratio Al^{+3}/F^-	Fluoride Found$^{(a)}$	Percent Found
1.0×10^{-2}	5.0×10^{-2}	5	5.5×10^{-4}	6
1.0×10^{-2}	1.0×10^{-1}	10	1.2×10^{-4}	1
1.0×10^{-3}	5.0×10^{-3}	5	9.6×10^{-4}	100
1.0×10^{-3}	1.0×10^{-2}	10	7.2×10^{-4}	72
1.0×10^{-4}	1.0×10^{-4}	1	9.8×10^{-5}	98
1.0×10^{-4}	1.0×10^{-4}	1	1.0×10^{-4}	100
1.0×10^{-4}	2.0×10^{-4}	2	1.0×10^{-4}	100
1.0×10^{-4}	2.0×10^{-4}	2	9.9×10^{-5}	99
1.0×10^{-4}	5.0×10^{-4}	5	1.0×10^{-4}	100
1.0×10^{-4}	1.0×10^{-3}	10	1.0×10^{-4}	100
1.0×10^{-4}	2.2×10^{-3}	22	9.4×10^{-5}	94
1.0×10^{-4}	7.2×10^{-3}	72	7.0×10^{-5}	70
1.0×10^{-4}	1.2×10^{-2}	120	6.6×10^{-5}	66

(a) Expressed as moles/liter.

(b) Added as sodium fluoride.

(c) Added as aluminum sulfate.

aluminum/fluoride ratio. For fluoride at the 10^{-4} molar level, accurate measurements were possible in the presence of a ten-fold excess of aluminum, while the measurement was only 5% low with a twenty-fold excess. At the 10^{-3} M fluoride level, a ten-fold excess of aluminum produced a fluoride measurement that was low by over 25%; but with a five-fold excess, an accurate measurement possible.

The absolute amount of aluminum that can be tolerated decreases as the amount of fluoride to be measured decreases. However, it does not appear to decrease as rapidly. Thus at the 10^{-3} M fluoride level, 5×10^{-3} M aluminum can be tolerated; at 10^{-4}, at least 1×10^{-3} M aluminum does not interfere. This effect can also be seen by comparing the effects of 1.0×10^{-2} M and 7.2×10^{-3} aluminum at fluoride concentrations of 10^{-3} and 10^{-4} M, respectively. In each case the amount of fluoride measured was about 30% low. Consequently, it appears that for solutions containing large amounts of fluoride, the tolerance for aluminum can be improved by performing a dilution of the sample.

Iron also interferes in the direct electrode measurement, but to a significantly less extent than does aluminum. The results of a number of measurements to evaluate the interference due to iron are shown in Table 4. At the 10^{-4} M fluoride level, a 100-fold excess of iron does not introduce significant error into the measurement.

Anions such as silicate, sulfate, and phosphate, which might be expected in field samples, were studied; their effects on the direct electrode measurement are shown in Table 5. Silicate at the 1 M level has no measurable effect on the measurement of 10^{-4} M fluoride. Large excesses of phosphate and sulfate could also be tolerated. In these measurements the citrate was not acting as a complexant; it only served to adjust ionic strength. As a result, the citrate level could be reduced to 0.1 M without significantly affecting the insensitivity of the electrode to these anionic interferences.

Table 4

Effect of Iron (III) on Fluoride Measurement in 0.5 Molar Citrate Buffer

Fluoride Added[a,b]	Iron Added[a,c]	Mole Ratio Fe^{+3}/F^-	Fluoride Found[a]	Percent Found
1.0×10^{-4}	1.0×10^{-4}	1	0.99×10^{-4} 1.02×10^{-4}	99 102
1.0×10^{-4}	3.0×10^{-4}	3	1.03×10^{-4}	103
1.0×10^{-4}	5.0×10^{-4}	5	1.03×10^{-4}	103
1.0×10^{-4}	1.0×10^{-3}	10	1.02×10^{-4} 0.99×10^{-4}	102 99
1.0×10^{-4}	1.0×10^{-2}	100	0.97×10^{-4}	97
1.0×10^{-4}	1.0×10^{-1}	1000	0.76×10^{-4}	76

(a) Expressed in moles/liter.

(b) Added as sodium fluoride.

(c) Fe added as $Fe(NH_4)(SO_4)_2\ 12 \cdot H_2O$

Table 5

Effect of Other Potential Interferences on Fluoride Electrode Measurements Using Citrate Buffer

Citrate Level(a)	Interference(c)	Fluoride Added(a,b)	Mole Ratio Interference/F$^-$	Fluoride Found(a)	Percent Found
0.5	Silicate	1.0×10^{-4}	1	1.0×10^{-4}	100
			10	1.0×10^{-4}	100
0.1	Silicate	1.0×10^{-4}	100	9.8×10^{-5}	98
			1000	1.03×10^{-4}	103
			10,000	1.03×10^{-4}	103
0.1	Sulfate	1.0×10^{-4}	1000	9.3×10^{-5}	93
0.1	Phosphate	1.0×10^{-4}	1000	1.0×10^{-4}	100

(a) Expressed as moles/liter

(b) Added as sodium fluoride

(c) Interferences added as sodium silicate, sodium sulfate, and disodium hydrogen phosphate.

Table 6

Comparison of Fluoride Electrode and Zr-SPADNS Measurement Methods[a]

Distillation	Species	Moles F	Percent Fluoride Recovery	
			Electrode	Zr-SPADNS
Sulfuric (to 210°C)	NaF	1.0×10^{-5}	101	138
		1.0×10^{-4}	98	106
		1.0×10^{-3}	97	97
Perchloric (at 135°C)	CaF_2[b]	1.1×10^{-4}	88	86
	CaF_2[c]	1.1×10^{-4}	86	83
	Cryolite	2.1×10^{-4}	86	81
	Phosphate Rock	1.1×10^{-4}	100	100

(a) Comparative analyses performed on aliquots of the same sample of distillate.

(b) Sample also contained 1.0 g PbO.

(c) Sample also contained 1.0 g Fe_2O_3.

2. Comparison of the Fluoride Electrode with the Zirconium-SPADNS Method

Distillations of a variety of samples were performed, and the collected distillates were split and measured by the fluoride electrode as well as by the zirconium-SPADNS method. A comparison of the results obtained is shown in Table 6. For sulfuric acid distillates, agreement is excellent at 10^{-3} M fluoride. However, at lower fluoride levels, the Zr-SPADNS results become progressively higher probably due to the positive interference of small amounts of sulfuric acid carried over in the distillate at high temperatures. The sulfuric acid carried over has no effect on the electrode measurement even at the 10^{-5} M fluoride level (see Table 5).

With the perchloric acid distillates, there is good general agreement. Recoveries, as determined by both methods, are low for the calcium fluoride and cryolite samples. It is generally known that a single distillation from perchloric acid at 135°C will not yield quantitative fluoride recovery from cryolite; a pre-distillation from H_2SO_4 at 165°C is required to effect the separation of fluoride from aluminum. To stimulate field samples, Pb^{+2} and Fe^{+3} were added to the calcium fluoride samples. The presence of large excesses of these metals probably caused a low fluoride recovery for calcium fluoride during the distillation step. Therefore, the low recovery appears to be due to incomplete fluoride evolution from distillations and is probably not related to the measurement procedures per se.

c. Inter-Laboratory Comparison of the Fluoride Electrode

To provide a realistic evaluation of the possibility of making fluoride measurements via the fluoride electrode directly on a field sample, a series of samples taken at diammonium phosphate and phosphoric acid plants were split and were independently analyzed in this laboratory and in the laboratories of EPA. With only two exceptions the results, shown in Table 7, are in excellent agreement. Samples C-1 and C-2 were

TABLE 7

TOTAL SOLUBLE FLUORIDES IN EPA SAMPLES BY DIRECT ELECTRODE MEASUREMENT

Sample Designation	ADL Results		EPA Results	Remarks
	moles/1	µg/ml	µg/ml	
165PF + 166PF + 167PF, C-1*	5.0×10^{-2}	950	960	strongly acidic
168PF + 230PF, D-1	$1.6_2\times10^{-3}$	31	29.5	
172PF + 232PF, F-1	3.3×10^{-3}	63	62	
187PF + 238PF, C-2*	4.5×10^{-2}	860	944	strongly acidic
189PF + 234PF, D-2	7.4×10^{-4}	14	13.9	
91PF + 192PF + 193PF, E-2	$1.4_4\times10^{-3}$	27	27	
270PF + 271PF + 272PF, R-2	2.7×10^{-3}	51	52.4	very alkaline
273PF + 339PF, K-2	5.2×10^{-3}	99	98	moderately acidic
275PF + 342PF, M-2	3.9×10^{-4}	7.4	7.2	
277PF + 341PF, P-2	$1.4_8\times10^{-4}$	2.8	2.7	
F Std., 10 µg/ml, #11**	5.3×10^{-4}	10.1	10.0	very alkaline

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* Sample stability in doubt, see text.

** Supplied as known standard by EPA, concentration derived from ADL calibration curve.

strongly acidic and it is not unlikely that fluoride was lost from these two samples during transit, storage, and handling.

d. Conclusions

The results of these studies support the earlier conclusions from our literature survey that the fluoride electrode is capable of producing precise and accurate results quickly and easily without the need for highly trained or experienced personnel. If a complexing buffer is used, significant excesses of aluminum and iron in solution can be tolerated. If intolerably high amounts of interfering cations are present, a separation is necessary, but after a separation has been performed, the fluoride electrode appears to be as good as or better than other techniques for fluoride ion measurement.

2) Studies of Techniques for Fusing Particulates Experiments to compare a variety of fusion fluxes were performed using cryolite ($3NaF \cdot AlF_3$) as a model compound because it is one of the more intractable fluoride-containing compounds which one might expect to encounter in field samples. Fluxes evaluated included the following:

- mixed carbonates (sodium/potassium eutectic)
- sodium hydroxide
- sodium hydroxide/borax
- sodium carbonate/borax
- mixed carbonate/borax

The admixtures of borax (sodium borate) were tested since borax has been reported by some industry sources to aid in the dissolution of refractory fluoroaluminates.

Mixed carbonates and sodium hydroxide were equally effective for fusing cryolite. The mixed carbonates were found to be easier to use than sodium hydroxide.

a. Apparatus and Procedure All fusions were carried out in covered, 50-ml nickel crucibles over a Fisher burner operating on natural gas/air.

The crucibles were cleaned between each test by fusing fresh portions of mixed carbonate flux to ensure that no residual fluoride remained in the crucible. After cooling, the melt was removed by rapping the inverted crucible on a hard surface, and the crucible was washed carefully with distilled water.

After the crucible had been cleaned, a portion of the requisite amount of flux to be tested was first placed in the cleaned crucible and the sample was added, followed by the remainder of the flux. The solids were then mixed, the crucible covered, and the fusion carried out at medium red heat, approximately 700-750°C. The usual fusion time was 10 minutes, but some 30-minute tests were performed to determine if a longer fusion was necessary; fusions were timed from the point when all of the flux had melted. After fusion, the crucibles were cooled to room temperature before treating the fusate further.

About half of the fluoride measurements for the fusion tests were performed with the specific ion electrode directly on solutions of the fusate containing 0.5 M citrate. The amounts of each flux were chosen so that when the cooled melt was dissolved in water, neutralized with citric acid to a pH of ca.7 as indicated by bromthymol blue, and diluted to 50 ml, the final citrate concentration would be 0.5 M.

The remaining fusate samples were distilled from sulfuric acid and the distillate measured with the fluoride electrode after pH adjustment and addition of sodium citrate. Complete details of this procedure is included in Part 3 of this Section.

b. Results and Discussion The compositions of the five fluxes used in these experiments are shown in Table 8. Fluoride recoveries are shown in Table 9. Initially, fusions were performed using a cryolite sample (cryolite A) which, in retrospect, appears to have been impure. The recoveries in Runs 3, 4, and 8-12, using three different fluxes all range from 84-90% with an average recovery of 87%. Subsequent to these measurements, a new sample of cryolite (cryolite B) was obtained. It was fused

TABLE 8

Description of Flux Compositions

Code	Type	Chemical	Weight(g)
A	Sodium Carbonate/Borax	Na_2CO_3	3.4
		$Na_2B_4O_7 \cdot 10\ H_2O$	1.1
B	Mixed Carbonate/Borax	Na_2CO_3	1.5
		K_2CO_3	1.9
		$Na_2B_4O_7 \cdot 10\ H_2O$	1.1
C	Sodium Hydroxide/Borax	NaOH	2.8
		$Na_2B_4O_7 \cdot 10\ H_2O$	0.9
D	Mixed Carbonate	Na_2CO_3	2.0
		K_2CO_3	2.5
E	Sodium Hydroxide	NaOH	3.0

TABLE 9

Fluoride Recoveries from Test Fusions of Cryolite(a)

Run No.	Fusion Time (min)	Flux(b)	Cryolite(d)	Fluoride Added (moles)(c)	Percent Recovery	Average
1	10	A	A	2.4×10^{-5}	87	81
2	10	A	A	2.0×10^{-4}	74	
3	10	B	A	2.2×10^{-4}	88	88
4	30	B	A	2.2×10^{-4}	88	
5	10	C	A	2.0×10^{-4}	77	74
6	30	C	A	2.1×10^{-4}	70	
7	30	D	A	2.1×10^{-4}	100	92
8*	10	D	A	1.9×10^{-4}	87	
9*	10	D	A	2.1×10^{-3}	89	
10	30	E	A	2.1×10^{-4}	84	86
11*	10	E	A	1.8×10^{-4}	86	
12*	10	E	A	2.0×10^{-3}	90	
13*	10	D	B	2.0×10^{-4}	99	100
14*	10	D	B	2.0×10^{-4}	100	
15*	10	E	B	2.1×10^{-4}	97	97

(a) - Direct electrode measurement on dissolved fusate expect for runs indicated (*) where the fusate was distilled from H_2SO_4 prior to electrode measurement.

(b) - Description of fluxes in Table 8.

(c) - Assuming Cryolite was 100% $3\ NaF \cdot AlF_3$.

(d) - See text

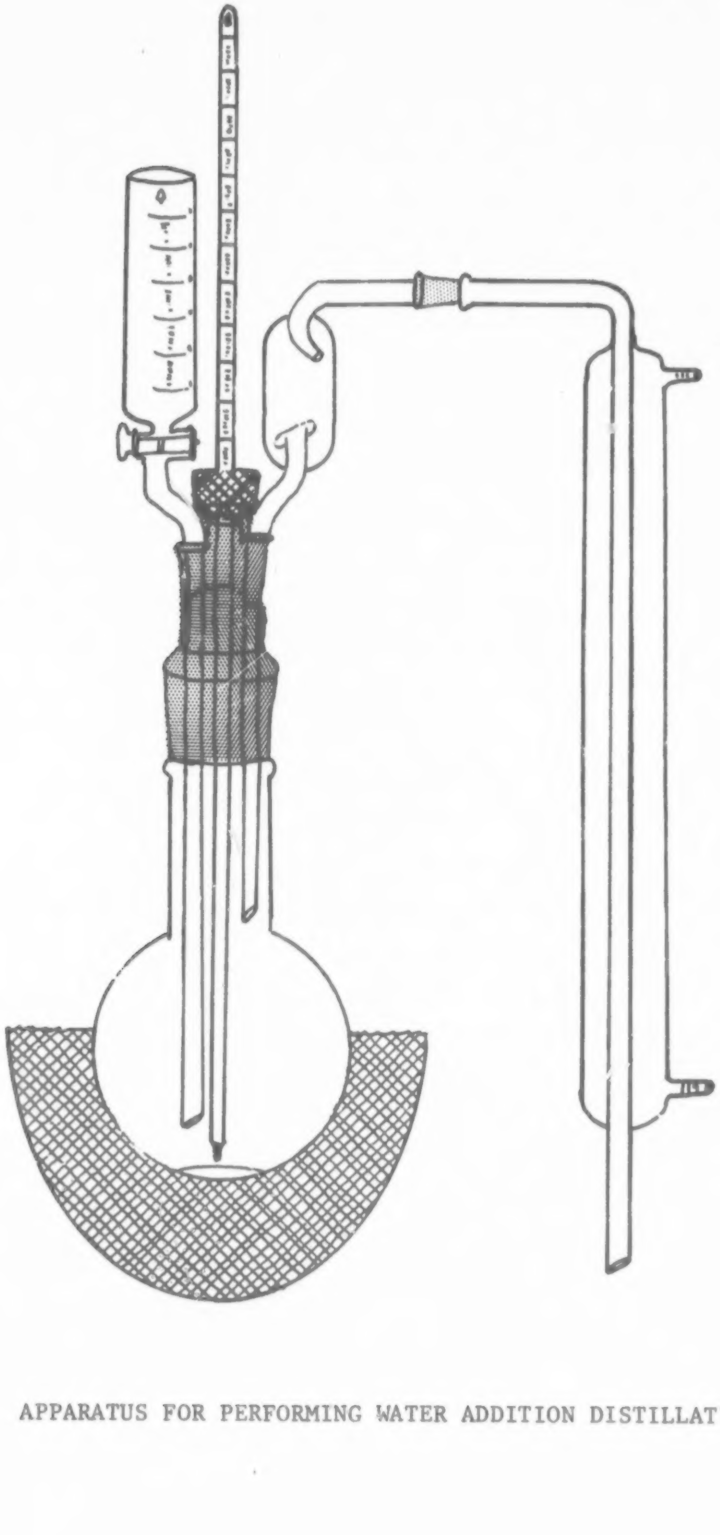

FIGURE 12 APPARATUS FOR PERFORMING WATER ADDITION DISTILLATIONS

with both sodium hydroxide and mixed carbonates (Runs 13-15) and very nearly 100% recovery was obtained. We are, therefore, quite certain that the first cryolite was probably about 87% pure; the single 100% recovery for this material in Run 7 is most likely in error.

An examination of the results in Table 9 shows that sodium hydroxide, mixed carbonates, and mixed carbonate/borax yield equivalent recoveries. The inclusion of borax in the flux did not increase fluoride recovery from cryolite. In fact, with the sodium hydroxide/borax flux (Runs 5 and 6), the opposite may be true. The reason for lower recovery in those two runs is unclear. However, it was observed that this flux corroded the nickel crucibles very rapidly, and loss of fluoride could have conceivably accompanied corrosion. In the three cases examined, there seems to be no significant increase in fluoride recovery when the time of fusion is extended from 10 min. to 30 min.

One can conclude that the mixed carbonate flux and the sodium hydroxide flux are equally capable of effecting complete fusion. We have found in the course of these experiments, however, that the mixed carbonate flux is more convenient to use since the fusion proceeds at a lower temperature. The mixed carbonates have less of a tendency to creep up the sides of the crucible and they generally contain less water. The latter point is significant, because water trapped in the flux is evolved with sputtering when the fusion is initiated and may lead to mechanical loss of the sample.

3) Evaluation of Distillation Procedures

a. Introduction Two distillation procedures using sulfuric acid were studied as potential alternates to the tedious Willard-Winter perchloric acid distillation. The first approach involved the dropwise addition of water during the H_2SO_4 distillation to hold the pot temperature more or less constant. This "water-addition distillation" is similar to the constant temperature distillation for sulfuric acid at 165°C that is widely used prior to a perchloric acid distillation when one is dealing with "hard to distill" samples.

The second approach, termed a "direct distillation," involved the addition of the sample to a sulfuric acid/water solution in the still pot, applying heat, and allowing the distillation to proceed with no further additions to the pot. This latter approach is essentially the one recommended in the ASTM Method for Fluoride Ion in Industrial Water (D1179-68).

Tests on a variety of samples representative of those expected to be found in process effluent samples showed that both of the sulfuric distillations could be operated to produce essentially quantitative recovery. In general, recoveries from the sulfuric acid distillations were as good as, and sometimes better than, the Willard-Winter perchloric acid distillation. Because it is the simpler procedure and produces a lower reagent blank, the direct distillation is recommended over the approach involving continuous water addition.

b. Apparatus and Procedure The apparatus used for the constant temperature water addition distillations (from both sulfuric acid and perchloric acid) is shown in Figure 12. It consists of a 300-ml distillation flask equipped with an addition funnel, a thermometer, and a Kjeldahl-type spray trap leading to a straight condenser mounted nearly vertical. The distillation flask was heated by a heating mantle and the spray trap and connections to the condenser were wrapped with electric heating tape and insulation to prevent condensation. In practice, the sample and some 4 mm diameter soft glass beads were added to the flask, the system was closed, and the sulfuric acid added from the addition funnel. After heat had been applied and the temperature had reached the desired value, water was added from the addition funnel at a rate which held the temperature at the desired value. For collection of the distillate, the condenser outlet was kept just beneath the surface of dilute (approximately 0.05 m) sodium hydroxide solution to which phenolphtalein had been added. Thus, the fluorides were trapped in an alkaline medium, and the indicator showed if excess acid had distilled over and lowered the pH.

It was decided to measure the distilled fluorides via the specific ion electrode procedure using 0.1 M citrate buffer to compensate for any pH and ionic strength variations which could have resulted from acid carry-over. Thus, after the distillation was complete, the requisite volume of 1.0 molar sodium citrate was added along with a few drops of bromthymol blue indicator. The solution was neutralized to the green of the indicator with 6 M hydrochloric acid and was then diluted to a known volume with water. The fluoride content was measured using the fluoride electrode and concentrations were determined from a calibration curve prepared from sodium fluoride in the same buffer.

The apparatus used for the initial direct distillation (without water addition) experiments was the same apparatus that had been used for the preceding distillations with water addition. The samples, whether fused or just mixed with the carbonate flux material, were transferred to the flask, together with a total of 60 ml of distilled water and a few soft glass beads. The flask was then coupled to the distillation train, and a total of 70 ml concentrated sulfuric acid was added carefully via the addition funnel. This water/acid ratio was selected because its initial boiling point was around 155°C. The solution temperature generally rose to approximately 140°C during acid addition. The solution was then heated with the heating mantle at constant power, and boiling generally commenced around 155-160°C.

The distillate was collected in 0.05 molar sodium hydroxide containing phenolphthalein indicator, and extra hydroxide was added as required to keep the solution alkaline. The distillate was collected in two 25 ml fractions. At the end of the second fraction, the pot temperature had reached 240°C, and excessive amounts of acid began to appear in the distillate as indicated by the need to add increasing amounts of sodium hydroxide to keep the distillate alkaline.

To study further the effect of distillate volume collected on fluoride recovery, a series of distillations were performed using the same apparatus, but the volumes of water and acid were increased by 50% to 90 and 105 ml, respectively. The distillate volume collected was increased proportionately; a total of 75 ml of distillate was collected in three equal fractions. Pot temperatures at the end of each 25 ml fraction were approximately 175°C, 210°C and 240°C. Relatively high heating mantle voltages (approximately 100 volts) were used; the fractions came off in about 20 minutes each.

The distillation incorporated in ASTM Method D1179-68 is also a direct distillation but involves a further scale-up of pot volume and amount of distillate collected. Because it could have a potentially lower fluoride blank and could be somewhat simpler to use than the previous direct distillation procedure, the ASTM method was evaluated as written and also with modification to go to a higher final pot temperature.

The apparatus used for this direct distillation was essentially the same as described in ASTM D1179-68. It was quite similar to the apparatus shown in Figure 12 except that a larger, one-liter still pot was used. A Graham condenser was substituted for the straight condenser, and the addition funnel was omitted.

The procedure for the ASTM-type direct distillation involved first charging the pot with a mixture of 200 ml concentrated sulfuric acid and 400 ml of water. The acid solution was then distilled until the pot temperature reached a predetermined temperature (180°C in the ASTM method; 210°C in our final method). Due to the higher efficiency of the Graham condenser, an alkaline receiving solution was not used, and the tip of the condenser was not immersed beneath the surface of the liquid in the receiver.

After the initial distillation of the acid solution, the pot was cooled to under 40°C and the sample, together with 300 ml of distilled water, was added slowly with careful mixing. Heat was then applied, and the sample distilled until the pot reached the same maximum temperature as used during the preceding cleanup distillation.

used during the preceding cleanup distillation.

Preparation of the collected distillate for measurement using the fluoride electrode was done in the same way as described above for the water addition distillations. However, as an alkaline collecting solution was not used in this procedure, the collected distillate was weakly acidic, and the citrate buffer alone was usually capable of bringing the solution to the proper pH for measurement.

In the ASTM-type direct distillation procedure, the acid in the distilling pot can be reused for subsequent samples until the metal content becomes high enough to significantly retard the evolution of fluoride. In this work the pot was recharged after every third sample.

c. Results and Discussion

1) Water Addition Distillation The results of a series of water addition distillations from sulfuric acid performed at several temperatures on a variety of sample types are summarized in Table 10. In order to better understand the evolution of fluoride as the distillation proceeded, the distillate was collected in separate, successive, 50-ml fractions and the fluoride in each was determined.

When aluminum is present in the sample to be distilled, it tends to form soluble complexes with fluoride and thus reduces the fluoride vapor pressure at a given temperature. The slower evolution of fluoride in the presence of aluminum can be seen by comparing Runs 3 and 4 with the distillation of a phosphate rock sample in Run 9. Evolution of fluoride from the phosphate rock was virtually complete at a temperature somewhat less than 165°C after the first 50-ml fraction of distillate had been collected, but 4-6% of the fluoride from the cryolite sample was found in the second 50-ml fraction.

Increasing the distillation temperature markedly increased the rate of fluoride evolution from a given sample type. This effect can be observed by comparing Runs 1 and 2 with Runs 3 and 4. At the lower temperature, 8 to 10% of the fluoride was found in the third fraction, while at 165°C evolution was virtually complete in the first 100 ml. Although there is a large difference in the amount of added fluoride in Runs 1 and 2 as compared to 3 and 4, we believe it is temperature rather than sample size that affects distillation recoveries. Runs 5 and 6, which started with only 100μ moles of fluoride yields results more like those of 1 and 2 than like 3 and 4.

TABLE 10

Water-Addition Distillation of Fused Solid Samples

Run	Material	Temp (°C)	Fluoride Added (μ moles)	-------Fluoride Found in Distillate Fractions (μ moles)[a]----					Percent Recovery
				1st 50 ml	2nd 50 ml	3rd 50 ml	4th 50 ml	Total	
1	Cryolite	130-135	1750	1260 (72%)	310 (18%)	140 (8%)	NC[d]	1710	98
2	"	130-135	1720	1050 (61%)	420 (24%)	180 (10%)	NC	1650	96
3	"	165	201	190 (95%)	13 (6%)	NC	NC	201[c]	100
4	"	165	210	195 (93%)	9 (4%)	NC	NC	206[c]	96
5	NaF + Al(III)[b]	140	100	73 (73%)	23 (23%)	13 (13%)	NC	107[c]	107
6	"	140	100	79 (79%)	18 (18%)	5 (5%)	NC	100[c]	100
7	"	140	20	3.5 (18%)	15 (75%)	2.2 (11%)	< 0.1	19[c]	95
8	Blank	140	0	1.4	0.3	0.3	< 0.1	2.0	-
9	Phos. Rock	150-165	108	108 (100%)	2 (2%)	< 1	< 1	108[c]	100

---

[a] - Percentages in parentheses are the percentages of the amount added that was found in each distillate fraction.

[b] - Ten-fold mole excess of Al(III) added as aluminum salt.

[c] - Total recovery corrected for reagent blank of 2 μ moles.

[d] - NC - fraction not collected.

The effect of aluminum in depressing vapor pressure and increasing distillation time appears to be more or less independent of the aluminum/fluoride ratio. If one compares Runs 1 and 2 with Runs 5 and 6, the profile of percent fluoride distilled as a function of distillate volume collected appears quite similar, even though in the cryolite samples the aluminum/fluoride ratio was about 1:6, while in Runs 5 and 6 the aluminum/fluoride ratio was 10:1.

In the water distillation, the distillation time and consequently the amount of operator attention required increases in proportion to the amount of total distillate to be collected. From this standpoint, it would be desirable to operate at the highest temperature possible to minimize distillation time. However, it was observed that at temperatures very much in excess of 170°C, the entering water droplets tended to explode violently upon hitting the surface of the hot acid, and to maintain a relatively constant temperature, required the undivided attention of the operator.

Since the measurement of fluoride with the ion specific electrode is not affected by varying small amounts of sulfuric acid that might occasionally distill over, it was apparent that the requirements for close control of temperature could be relaxed. It was found that if the temperature were allowed to vary between 140-170°C, the explosive water/acid reaction could be minimized, and only a periodic check of temperature and minor adjustment of water addition rate was required. Under these conditions, the only concern then was that sufficient distillate be collected to insure complete fluoride recovery.

To determine the amount of distillate collection required under worst case conditions, three experiments were performed at a carefully controlled temperature of 140°C. As essentially quantitative recovery was obtained after collecting 150 ml of distillate (Runs 5-7), it seemed reasonable to assume that one should be able to obtain quantitative recovery at pot temperatures anywhere within the range of 140-170°C for a total of 200 ml of distillate collected. In Run 7, the fourth fraction was found to contain an insignificant amount of fluoride, lending support to this assumption.

2) Small-Volume Direct Distillations from Sulfuric Acid The water-addition distillation from sulfuric acid with only minimal temperature control is a less tedious procedure than the normal Willard-Winter distillation which requires very close control of temperature. The evaluation of an even

simpler procedure, a direct distillation with no additions to the pot while the distillation procedures, is described in this section. The distillation apparatus used for these initial experiments was the same as had been used in the preceding water-addition distillations.

Results of these initial direct distillations are shown in Table 11. For the first five runs, the pot was charged with a total of 130 ml of acid solution, and a total of 50 ml of distillate was collected. Recoveries of fluoride from NaF were excellent. The first run with cryolite, however, yielded only a 92% recovery. In all cases, 11-15% of the total fluoride added was recovered in the second 25 ml fraction.

In an attempt to improve the cryolite recovery, the volumes of water and acid charged as well as distillate collected were increased by 50%. Two cryolite samples and one sample of $NaBF_4$ were distilled under these conditions, with an average recovery of 86% for the former and 100% for the $NaBF_4$ sample.

The third fraction contained 1-3% of the total fluoride collected, which is hardly significant to the overall analysis. The low level of fluoride in this fraction provides assurance that significant amounts of fluoride will not be lost by failing to collect enough distillate.

A variety of species, including aluminum and iron, are known to retard the distillation of fluoride. Therefore, several distillations were carried out to evaluate potential interferences from phosphate, silicate, iron and aluminum. The results are presented in Table 12.

In order to see whether phosphoric acid might influence the rate of distillation of fluoride from solution, an addition and recovery of cryolite was carried out in the presence of a 1000-fold excess of phosphoric acid. The data suggest that the presence of phosphoric acid in the distillation pot may have resulted in a slight increase in the percentage of fluoride found in the first fraction, but this effect was not marked. Overall recovery is not significantly different from that found previously for cryolite alone.

The effect of large excesses of both aluminum and iron on the recovery of fluoride via direction distillation were studied using the appropriate metal

TABLE 11

RECOVERIES OF FLUORIDE USING SMALL-VOLUME DIRECT DISTILLATION FROM SULFURIC ACID

SAMPLE	FLUORIDE ADDED (µ moles)	FLUORIDE FOUND (µ MOLES)				PERCENT(d) RECOVERY
		1st 25 ml	2nd 25 ml	3rd 25 ml	Total	
NaF(a)	10	10.4	1.3	NC(c)	11.7	103
	10	10.2	1.1	NC(c)	11.3	99
NaF(b)	10	10.0	1.3	NC(c)	11.3	100
	10	9.9	1.5	NC(c)	11.4	101
Cryolite(b)	278	215	41	NC(c)	256	92
	197	162	30	3	195	99
	322	244	51	2	297	92
$NaBF_4$(b)	358	250	100	10	360	100

(a) Mixed with 4.5 g mixed carbonates, not fused

(b) Fused with 4.5 g mixed carbonates

(c) Initial pot solution 60 ml H_2O plus 70 ml H_2SO_4, a total of 50 ml distillate collected. In other runs, initial pot solution 90 ml H_2O plus 105 ml H_2SO_4, a total of 75 ml distillate collected.

(d) Percent recoveries computed from total recovery after correcting for a reagent blank of 1.4 µ moles fluoride.

TABLE 12

EFFECT OF POTENTIAL INTERFERENCES ON DIRECT DISTILLATION - 75 ML DISTILLATE

FLUORIDE		OTHER SPECIES		MOLE RATIO	FLUORIDE FOUND (μ MOLES)				
SPECIES[a]	AMOUNT (μ MOLES)	TYPE[b]	AMOUNT (M MOLES)	OTHER/FLUORIDE	1st 25ml	2nd 25ml	3rd 25ml	TOTAL	PERCENT[c] RECOVERY
Cryolite B	214	H_3PO_4	200	1000	182	11	NA[e]	193	90
NaF	10	Al (III)	10	1000	6.2	4.5	1.1	11.8	104
NaF	10	Al (III)	10	1000	7.6	3.1	0.2	10.9	95
NaF	10	Fe (III)	10	1000	8.6	0.7	0.3	9.6	82
NaF	10	Fe (III)	1	100	9.4	0.8	0.2	10.4	90
NaF	10	Silicate	10	1000	2.3	2.1	1.6	6	46
NaF	10	Silicate	1	100	6.5	2.6	0.5	9.6	82
NaF[d]	10	Silicate	1	100	5.5	2.8	0.4	8.7	73

(a) All samples mixed with 4.5 g mixed carbonates, only cryolite was fused

(b) Interfering species added as aluminum sulfate, ferric ammonium sulfate, and sodium metasilicate

(c) Corrected for reagent blank (acid and carbonates only) of 0.14×10^{-5} moles F^-

(d) 1.0×10^{-3} moles $MgSO_4$ added in attempt to precipitate silicate

(e) Fraction not analyzed

salt and sodium fluoride. In these experiments, aluminum was found not to retard fluoride evolution, whereas iron seemed to have an effect, i.e., an increase in the amount of iron resulted in a poorer recovery. It must be noted that variations in the 1.4μ mole reagent blank at the 10μ mole sample level can reduce the statistical significance of these findings. However, we do believe the effect of 10μ moles of iron on fluoride recovery is real, and the possible influence of 1μ mole iron is reason enough to keep iron concentrations below 1μ mole.

In comparison to the above, the deleterious effects of large amounts of silicate are quite significant. The addition of acid to the water soluble silicate results in rapid formation of a gel of silicic acid. Fluoride may be absorbed into this gel and trapped. Also, portions of this gel are splashed up onto the upper area of the flask during boiling away from further contact with the acid. An attempt to precipitate the silicate as magnesium silicate was of no avail and indeed may have resulted in still poorer recovery.

3) ASTM-Type Direct Distillation from Sulfuric Acid The ASTM-type direct distillation procedure was first evaluated by distilling five fused cryolite samples according to ASTM Method D1179-68. The results of these experiments are shown in Table 13; an average recovery of about 92% was observed for the five runs. The aluminum/fluoride ratio varied from 0.17 to 5.0 and appeared to have no significant effect on the recovery.

With the water-addition distillation discussed previously, recoveries closely approaching 100% could be obtained for the same cryolite sample. In an attempt to achieve better recovery with the direct distillation, it was decided to let the distillation proceed to a higher final pot temperature. The distillate was collected in two fractions--that which came over at pot temperatures up to 180°C and that which came over between 180 and 210°C. The results of this experiment are presented in Table 14; for a variety of fluoride levels and aluminum/fluoride ratios, approximately 95% of the added fluoride was recovered in the first fraction. By allowing the distillation to proceed to 210°C, an overall average recovery of 99% was achieved.

Similar experiments were performed on actual field samples from several industries of concern in this work. The results presented in Table 15 show

TABLE 13

RECOVERY OF FLUORIDE FROM FUSED CRYOLITE IN PRESENCE OF ALUMINUM VIA 180°C ASTM DISTILLATION

Run	Al Present (μmoles)	F added[(a)] (μmoles)	F Found (μmoles)	Percent Recovery
1	40	232	205	88
2	60	124	118	95
3	100	251	235	94
4	1000[(b)]	138	118	86
5	1000[(b)]	203	194	96

(a) Added as Cryolite B (see text) and assumed to be 100% $3NaF \cdot AlF_3$. Each sample was fused with 4.5g mixed carbonates (Na_2CO_3- CO_3).

(b) Excess Al(III) added as aluminum sulfate.

TABLE 14

COMPARISON OF DIRECT DISTILLATION RECOVERIES AT 180 and 210°C

Fluoride Added[a] (μ moles)	Ratio[b] Al/F	Fluoride Found (μ moles) < 40 - 180°C	Fluoride Found (μ moles) 180 - 210°C	Fluoride Found (μ moles) Total	Percent Recovery
100	10	95	4	99	99
10	100	9.9	0.2	10.1	101
100	10	93	5	98	98
1000	1	950	23	973	97

(a) Added as sodium fluoride

(b) A constant amount of Al(III), 1000 μ moles, was added as aluminum sulfate.

TABLE 15

RECOVERIES OF FLUORIDE FROM PORTIONS OF PARTICULATE FIELD SAMPLES VIA DIRECT DISTILLATION AND ELECTRODE MEASUREMENT

Sample Description	Fluoride Found (μ moles) 180° Fraction	180-210° Fraction	%F in 180° Fraction
Aluminum Facility			
Filter catch, ∿ 19% of total sample	178	3.0	98
Water probe wash, ∿ 21% of total sample	98	1.9	98
Acetone probe wash, 50% of total sample	64	1.0	93
Glass Facility			
Filter catch, 13% of total sample	205	11	95
Probe wash, 25% of total sample	8	∿ 0.1	99
Phosphate Rock			
Standard sample	69	2.1	97
	73	2.5	97

that a 2-5% improvement in recovery was obtained by extending the maximum distillation temperature from 180 to 210°C; furthermore, the results suggest that the direct distillation can provide good quantitative recovery under these conditions.

In carrying out the direct distillation to 210°C, a small amount of sulfuric acid is carried over at the high temperature range. While this has no effect on the fluoride electrode measurement, it can represent a significant positive interference at low fluoride levels when other measurement techniques such as Zr-SPADNS are used.

4) Comparison of the Two Sulfuric Acid Distillations and Comparison with the Willard-Winter Perchloric Acid Procedure To further compare the water addition and ASTM-type direct sulfuric acid distillations, four samples of standard phosphate rock were distilled using each procedure. These samples were first fused with mixed carbonates, and the final measurement was made with the fluoride electrode. The fluoride content of the phosphate rock had been determined by collaborative testing to be 3.80±0.018% (dry basis). The results of the distillation comparisons are shown in Table 16. For the water addition method, an average of 3.83% fluoride was obtained in very good agreement with the accepted value. Four determinations by the direct distillation procedure yielded an average fluoride content of 3.74%, within 2% relative of the accepted value. Although we have not been able to pinpoint the reason, we believe that the two low values determined by direct distillation result from a systematic error, perhaps the result of a leak in the apparatus. From our overall experience with them, we believe that the two techniques for distillation from sulfuric acid are capable of producing equally precise and accurate results.

In another series of experiments, distillation from sulfuric acid was compared with the "accepted" Willard-Winter perchloric acid distillation. Samples were chosen to be representative of those that might be encountered in the industries of primary concern to this work--calcium fluoride/lead (glass and ceramic industry), calcium fluoride/iron oxide (iron and steel), cryolite (primary aluminum), and standard phosphate rock (phosphate industry). The samples were fused with mixed carbonates prior to distillation and the final measurement was performed with the fluoride electrode. The results of this comparison are shown in Table 17. For three of the four samples the

TABLE 16

DISTILLATIONS FROM SULFURIC ACID

Comparison of 150 - 165°C Water Addition with 210°C Direct

Method	Sample (mg)[a]	Fluoride Found (μ moles)[b]	Weight % F
Water Addition	54.1	108	3.80
	57.4	115	3.81
	53.9	109	3.84
	54.7	111	3.86
Direct	51.2	103	3.82
	46.0	89.0	3.68
	35.0	70.0	3.80
	38.6	74.4	3.67

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[a] - Standard phosphate rock, 3.80% F (dry basis).

[b] - Electrode measurement. Corrected for reagent blank--water addition, 2 μ moles; direct 0.6 μ moles.

TABLE 17

COMPARISON OF SULFURIC AND PERCHLORIC ACID WATER ADDITION DISTILLATIONS

	H_2SO_4 Distillation (150 - 165°C)		$HClO_4$ Distillation (135°C)	
Sample	F Added (μ moles)	Percent Recovery	F Added (μ moles)	Percent Recovery
CaF_2 + 1.0 g PbO	99.5	82	106	92
CaF_2 + 1.0 g Fe_2O_3	99.4	97	105	90
Cryolite	210	97	208	87
Phosphate Rock	108	100	111	98

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sulfuric acid distillation yielded recoveries equal to or greater than those for the Willard-Winter distillation. The low recoveries with perchloric acid at 135°C for the samples containing iron and aluminum are not unexpected. For "hard to distill" samples such as these, a preliminary distillation from sulfuric acid is then subsequently distilled from perchloric acid at 135°C. Whether the 82% recovery for the simulated lead glass furnace sample by the sulfuric acid distillation is real or results from gross experimental error is not known. The fact that the distillation profile for the filter catch particulates obtained from a lead glass facility is not significantly different from the profile of other samples, as shown in Table 15, suggests that the 82% recovery may be due, at least, in part to experimental error.

d. Conclusions From the preceding experiments it is concluded that either the water addition or direct distillation from sulfuric acid are acceptable alternatives to the perchloric acid distillation if final fluoride measurement is performed with the fluoride ion specific electrode. The water addition distillation can be made less tedious by requiring that the temperature be controlled within the relatively wide range of 140-170°C; 200 ml of distillate must be collected to ensure quantitative recovery. To achieve quantitative recovery by the direct distillation, the pot temperature should be taken to 210°C. For direct distillation of small amounts of fluoride, measurement with the ion specific electrode is probably a definite requirement; there is sufficient sulfuric acid carryover at temperatures in excess of 180°C to interfere with most other measurement techniques.

Of the two sulfuric acid distillation techniques, the direct distillation is both easier and faster. It can be made almost completely automatic by incorporating a high-limit temperature sensor in the pot to turn off the heat once the 210°C temperature limit has been reached. The direct distillation does require a nonproductive pre-distillation of the initial acid charged into the pot. This limitation is not of major importance because once it has been pre-distilled, the pot can be used for a number of sample distillations. The pre-distillation has a distinct advantage in reducing the reagent blank to a lower level than is normally found in the water addition distillation.

e. Analysis of Field-Collected Samples

1) Primary Aluminum Samples To gain insight into the chemical nature of samples that one would encounter when performing fluoride analyses on process emissions, a variety of field samples were collected and studied in the laboratory. As there was a greater opportunity to obtain samples from a primary aluminum facility than from the other stationary sources, a larger number of aluminum industry samples were studied. Limited studies were also performed on samples provided by cooperating companies within the glass and phosphate rock processing industries.

Seven sets of samples were obtained from primary aluminum reduction plants. Sampling was carried out in a PHS-type sampling apparatus (the model supplied commercially by Research Appliance Company was used), consisting of a heated glass-lined probe, cyclone and filter assembly followed by a series of water impingers. A summary of the collected samples and sampling conditions is presented in Table 18. The six Series "A" samples were taken at the exit from an APC device while the set denoted "B" were collected ahead of the APC device.

The chemical nature of the impinger catch was studied by a variety of methods including the following:

- Dissolved Solids--drying at 105°C and ignition at 850°C.
- Fluoride--direct electrode measurement after buffering with 0.5 M citrate.
- Aluminum--atomic absorption spectrometry.
- Silicon--colorimetric analysis using molybdenum blue reagent.
- Total Acidity--potentiometric (pH) titration using 0.01 N NaOH.
- SO_2--iodometric titration.
- Chloride--mercurimetric titration.

The results of these studies are presented in Table 19. The ratio of aluminum to fluoride is less than unity in all cases. As has been shown previously for direct electrode measurement, a ten- to twenty-fold excess of aluminum over fluoride can be tolerated. The very high fluoride/silicon ratio observed for these samples strongly suggests that most of the gaseous fluoride enters the impinger at HF. A glass-line probe was used for obtaining these samples, and if it were converting all HF to SiF_4 as has been

TABLE 18

Summary of Samples and Sample Collection Data - Primary Aluminum Plant

Sample No	Dry Gas Volume (SCF)	Sampling Time (min)	Ave Stack Temp (°F)	Outlet Temp (°F)	Water Pickup Impinger (ml)	Water Pickup Silica Gel (g)	Filter Catch (mg)	Filter Type*
A-1	24.8	60	105	75	19	4	3	A
-2	23.9	60	95	75	22	8	1	C
-3	23.7	60	95	75	--	9	1	C
-4+	23.6	60	100	75	--	-	1	D
-5+	23.7	60	100	80	--	-	**	C
-6+	23.5	60	105	75	--	-	***	B
B-1	35.3	60	200	80	--	-	60	E

+ These runs were for filter catch only.

* Filter Types

A - 4" diameter MSA 1106B glass fiber

B - 2" diameter MSA 1106B glass fiber

C - 4" diameter Gelman "Acropore" membrane

D - 4" diameter Whatman No. 41 paper

E - 2" diameter Millipore HAW (0.45μ pore)

** Not tared.

*** Tare weight not available.

Table 19

Characterization of Impinger Catch from Primary Aluminum Plant Samples

Sample	Volume (ml)	Solids (mg)		Fluoride (mg)	Al (mg)	Si (mg)	Acid (mmoles)		SO_2 (mmoles)	Cl (mg)
		105°C	850°C				1st EP	2nd EP		
A-1	325	33	9	0.2	< 0.1	0.04	0.51	0.60	< 0.1	2
A-2	390	17	3.5	0.2	< 0.1	NA	0.78	1.4	0.2	NA
A-3	370	7	1	0.35	< 0.1	0.02	0.75	1.5	0.2	9
B-1	341	69	NA	126	NA	0.74	NA	NA	NA	41

NA - Not analyzed

postulated, significantly more silicon should have been found. It is also possible that hydrolysis of silicon tetrafluoride occurred after absorption into water yielding insoluble silicic acid which precipitated and was thereby missed in the silicon analysis. As there were no solids visible in the impinger solutions, this latter hypothesis should be valid for this group of samples.

The amount of total acidity exceeds that which can be accounted for on the basis of the measured fluoride, chloride and SO_2 contents. The titration curves indicated that the major acidic species had pH_a's of about 3 and 7. The pH_a of HF is about 3.5 so it is not likely to be the stronger acid; in any event, the fluoride level is only about 0.01 millimoles or about 2% of the amount of the stronger acid found. Since in subsequent studies it was found that the acidic material did not interfere in the fluoride measurement, no further attempt was made to provide a positive identification.

Several of the particulate filters were analyzed by emission spectrography; the results are presented in Table 20. In addition, the presence of chlorine and sulfur was detected by X-ray fluorescence. X-ray diffraction analysis yielded amorphous patterns; there was no evidence for the presence of any crystalline phases.

Separate containers of water and acetone probe washings were obtained as part of the Series B sample. These washings contained a significant amount of undissolved particulate which was filtered off and analyzed by X-ray methods. The results, shown in Table 21, indicate the presence of the same general inorganic elements that have been observed previously in the filter catch. However, crystalline alumina and cryolite were found in the probe washings. Apparently these materials are attracted to and adhere tenaciously to the probe walls during sample collection.

A summary of the distribution of fluoride and solids in the Series B sample is presented in Table 22. The following observations should be noted:

1. The insoluble fluoride particulate collected in the probe represents 7% of the total fluoride. X-ray diffraction data identifies the insoluble fluoride as cryolite.
2. The filter catch yields an amorphous diffraction pattern, yet accounts for 10% of the fluoride. This change in

Table 20

Emission Spectrographic Analysis of Filter Catch from a Primary Aluminum Plant

Level in Sample	A-4 (Paper)	A-5 (Membrane)	Paper Blank	Membrane$^{(a)}$ Blank	B-1 (Membrane)
> 10%	--	--	--	--	Al
0.3 - 3%	Al	--	--	--	Na
0.03 - 0.3%	--	Si	--	Si	Fe
0.01 - 0.1%	Na, Si	Al, Ti	--	--	--
30 - 300 ppm	Fe, Ga	--	--	--	Ca,Pb, Si, V
10 - 100 ppm	Ca, Ti	Ca, Fe, Ga, Na	Si	Ca	As, Cu, Ga, Sn, Ti
3 - 30 ppm	Cu, Mo, Ni, V	--	Ca, Fe	Fe, Na	Mg
1 - 10 ppm	--	Cu, Mo, Ni, V	Al, B, Cu, Na	Al, Cu	Ag, B

(a) This membrane blank was run using a filter of the type used for Sample A-5.

The B-1 membrane was from a second vendor, and no blank was run.

Table 21

X-Ray Analysis of Insoluble Particulate from Series B Probe Washings

Sample	Fluorescence	Diffraction
Water Wash	Ni, Ga, Fe Al, Ca, S, Ti	α-Al_2O_3, Na_3AlF_6
Acetone Wash	Ni, Fe Al, Ca, S, Ti	α-Al_2O_3

TABLE 22

FLUORINE AND SOLIDS DISTRIBUTION IN SERIES B SAMPLES COLLECTED FROM A PRIMARY ALUMINUM PLANT

	Probe Washings		Filter† Catch	Impinger Catch	Total
	Water	Acetone			
Initial Volume (ml)	100	144		341	--
Insoluble					
Solids (mg)	212	16		0	228
Fluoride (mg)	10	2.5		0	12
Soluble					
Solids (mg)	41	NA		69	110
Fluoride (mg)	15	0.5		126*	142*
Total					
Solids (mg)	253	16	60	69	398
Fluoride (mg)	25	3	18	126*	172
Distribution					
Solids (%)	68		15	17	
Fluoride (%)	16		10	74	

---

† Soluble and insoluble fractions were not determined

NA Not analyzed

* Includes HF which was driven off during the evaporation step

ratio of fluoride to solids from probe to filter suggests a preferential sorption of gaseous fluorides on the filter.

3. Altogether, the probe collects 16% of the total fluoride and 70% of the solids. Good probe cleaning techniques are therefore absolutely necessary to achieve quantitative results.
4. Since little silicon was found in the impingers, it is determined that HF is the only major gaseous fluoride species, accounting for at least 74% of the total fluoride.

2) Glass Furnace Samples Portions of a sample collected in the stack of a lead glass furnace were received from a cooperating company in the glass industry. They employed a heated stainless probe, glass fiber filter and water impingers. The analytical results obtained on the submitted samples are presented in Table 23. The majority (98%) of the fluoride was collected in the probe or on the filter. It is surmised that most of the fluoride was present as PbF_2, although X-ray analysis of the filter catch identified nothing other than PbO. The fact that 14% fluoride was collected in the probe implies that appropriate probe cleaning procedures are required.

3) Phosphate Rock Processing Samples To aid us in our understanding of potential problems associated with the analysis of actual field samples, a phosphate fertilizer company provided us with aliquots of samples collected from seven gas streams in the emission control system of a DAP plant. Sampling was carried out with a stainless steel probe followed immediately by a set of three impingers in series; the first impinger contained sulfuric acid for the collection of ammonia and the others contained dilute sodium hydroxide for collecting fluorides. At the conclusion of the sampling period, the contents of all three impingers were transferred into a single container.

The received samples were obviously acidic (pH < 1) and contained only a small amount ($\leq$ 1 mg) of particulate matter. This particulate was filtered off; no fluoride was detected in these solids. An aliquot of the filtrate was measured directly with the fluoride ion-specific electrode. Good recoveries of standard additions of fluoride were obtained, indicating

TABLE 23

FLUORIDE AND SOLIDS DISTRIBUTION IN GLASS INDUSTRY SAMPLES

	Probe Washings	Filter Catch*	Impinger Catch	Total
Initial Volume (ml)	140		280	
Insoluble				
Solids (mg)	41		0	41
Fluoride (mg)	0.6		0	0.6
Soluble				
Solids (mg)	NA		NA	--
Fluoride (mg)	4.8		0.7	5.5
Total				
Solids (mg)	--	1082	--	--
Fluoride (mg)	5.4	32	0.7	38.1

---

* Soluble and insoluble fractions were not determined.

that no significant amounts of interfering species were present in these solutions. The fact that all fluoride was water soluble and that levels of interfering species were tolerable, suggests that direct electrode measurements of DAP samples without pretreatment is feasible and should be carefully evaluated during field testing.

4) Direct Electrode Measurements on Field Samples The possibility of using the fluoride electrode for direct fluoride measurments of collected solution samples with no pre-treatment other than buffering is attractive. Direct measurement should be applicable in a variety of cases, particularly in the case of clear impinger solutions. To test this possibility, a number of fluoride standard addition and direct measurement experiments were performed on aliquots of the Series A and Series B sample solutions collected from a primary aluminum company; the results are shown in Table 24. Good recoveries were obtained for the impinger solutions as well as for the water probe washings. The results suggest that direct measurement of impinger solutions is not significantly affected by interfering species. That fact that fluosilicic acid, which was used for the Series "A" additions, could be recovered quite well indicates that the direct measurement should be feasible regardless of whether the fluoride enters the impinger as HF or as SiF_4. The good fluoride recovery from the Series "B" probe washings suggests that water soluble fluoride could be measured in an unfiltered sample without interference from dissolved cations. It is important to remember that particulate cryolite was present in the washings, and consequently, a total fluoride measurement would certainly require fusion and distillation.

E. Summary and Recommendations

Analytical methods development for the measurement of gaseous and particulate fluorides has been approached with a view of providing a procedure which is easily and reliably performed and has an accuracy and precision consistent with sample collection and storage procedures, but no worse than ± 10%. Based upon the review of the literature, discussions with workers in various industrial laboratories and our comprehensive laboratory studies that have been presented in this section, several methods have been identified as being consistently reliable. As the major laboratory effort

Table 24

Standard Additions of Fluoride to Primary Aluminum Plant Sample Solutions

	Amount of Fluoride (μmoles)				Difference	
Sample[a]	Initial	Added[b]	Total Expected	Found	Found Minus Expected	Percent Error
A-1-I	0.60	0.33	0.93	0.89	- 0.04	- 4%
	0.60	1.97	2.57	2.5	- 0.07	- 3%
	0.60	3.61	4.21	4.5	+ 0.3	+ 7%
A-2-I	0.79	0.33	1.12	1.0	- 0.02	- 2%
	0.79	1.97	2.76	2.7	- 0.06	- 2%
	0.79	3.61	4.40	4.6	+ 0.2	+ 4%
A-3-I	1.25	0.33	1.58	1.4	- 0.2	- 13%
	1.25	1.97	3.22	3.2	+ 0.01	0%
	1.25	3.61	4.86	4.7	- 0.2	- 4%
B-1-I	155	200	355	340	- 15	- 4%
B-1-W	325	200	525	490	- 15	- 7%
	325	400	725	690	- 35	- 5%

(a) Suffix I indicates impinger solution, W indicates water probe wash.

(b) Fluosilicic acid added to Series A Solutions, NaF to Series B solutions. Fluosilicic acid analyzed by acid/base titration.

was directed toward evaluating a variety of techniques for measuring soluble and insoluble fluorides in samples containing other potentially interfering compounds, there has been insufficient data obtained for any specific method to statistically specify method accuracy and precision, although probably reliable estimates have been given in the previous discussions of individual methods.

In striving for procedural simplicity in the hands of the inexperienced analyst, yet demanding a reliable and reproducible result, the use of the fluoride specific ion electrode for measuring fluorides in process effluent samples seems to be the optimum approach. Direct measurements on impinger solutions after buffering and addition of a metal complexant (0.5 M citrate has been shown effective) seems feasible in some cases, and should be compared critically to more rigorous sample fusion and distillation preparation procedures as part of a continuing field evaluation study.

The direct measurement approach seems most promising when either a particulate filter or electrostatic precipitator precedes the filter. Direct measurement may also be feasible for the phosphate rock industry; although both particulates and gases are collected in the impinger, the particulate fluorides are generally quite water soluble and thus would be included in an analysis for total fluorides.

In cases where insoluble particulate is present and a solubilization step is required, distillation from sulfuric acid, either with continuous water addition at temperatures in the range 140-170°C or directly according to ASTM Method D1179-68, but with a final pot temperature of 210°C should produce quantitative separation of fluoride from interferences prior to measurement with the fluoride electrode. If the water addition method is used, a minimum of 200 ml of distillate should be collected. The direct distillation is the preferred procedure because it is simpler and has a lower fluoride blank. The final fluoride measurement on the distillate using the fluoride electrode can be made easily; adjustment of pH and addition of 0.1 M citrate precedes the final measurement.

VI. LITERATURE REFERENCES

1. F. M. Robinson, G. I. Gruber, W. O. Lusk and M. J. Santy, "Engineering and Cost Effectiveness Study of Fluoride Emissions Control" EPA Report No. SN 16893.000 (January 1972).
2. C. C. Cook, G. R. Swany and J. W. Colpitts, "Operating Experience with the Alcoa 398 Process for Fluoride Recovery," JAPCA 21, 479-483 (1971).
3. W. S. Smith, Paper presented at the 60th Annual Meeting, APCA, Cleveland, Ohio (1967).
4. J. A. Dorsey and D. A. Kemnitz, "A Source Sampling Technique for Particulate and Gaseous Fluorides," JAPCA 18, 12-14 (1968).
5. L. A. Elfers and C. E. Decker, "Determination of Fluoride in Air and Stack Gas Samples by Use of an Ion Specific Electrode," Anal Chem 40, 1658-1660 (1968).
6. "Standard Sampling Techniques and Methods of Analysis for the Determination of Air Pollutants from Point Sources," Florida Department of Air and Water Pollution Control (January 1971).
7. G. L. Rounds and H. J. Matoi, "Electrostatic Sampler for Dust-Laden Gases," Anal Chem 27, 829-830 (1955).
8. G. H. Farrah, "Manual Procedures for the Estimation of Atmospheric Fluorides," JAPCA 17, 738-741 (1967).
9. R. H. Mandl, L. H. Weinstein, G. J. Weiskopf and J. L. Major, "Separation and Collection of Gaseous and Particulate Fluorides," Second International Clean Air Congress, Washington, D.C. (December 1970).
10. J. A. Dorsey, Environmental Protection Agency--Private Communication.
11. H. H. Willard and C. A. Horton, Anal Chem 22, 1190 (1950).
12. J. A. Dean, M. H. Buehler and L. J. Hardin, Assoc. Office Agr. Chemists 40, 949 (1957).
13. R. S. Allison, "The Determination of Small Amounts of Fluorine in Glass," J. Soc. Glass Technol., 37, 213-18 (1953).
14. J. J. Lingane, Anal Chem 39, 881 (1967).
15. H. H. Willard and C. A. Horton, Anal Chem 24, 862-865 (1952).
16. C. I. Grant and H. M. Haendler, Anal Chem 28, 415 (1956).
17. F. W. Dykes, G. L. Bouman, M. C. Elliot and J. E. Rein, U. S. Atomic Energy Comm. Rept. IDO-14405 (1959).

18. B. J. MacNulty, G. J. Hunter and D. G. Barrett, Anal Chim Acta 14, 368 (1956).

19. F. S. Grimaldi, Ingram and F. Cuttica, Anal Chem 27, 918 (1955).

20. APHA, "Standard Methods for the Examination of Water, Sewage and Industrial Waste," 11th ed. (1965).

21. E. Bellack and P. J. Schouboe, Anal Chem 30, 2032-2034 (1958).

22. W. H. Wharton, Anal Chem 34, 1296-1298 (1962).

23. Fisher Scientific Co., Application Data Sheet L-174 Lanthanum Chloranilate.

24. Fisher Scientific Co., Application Data Sheet T-401 Thorium Chloranilate.

25. M. A. Leonard and T. S. West, J. Chem. Soc., 4477 (1960).

26. M. S. Frant and J. W. Ross, Jr., "Electrode for Sensing Fluoride Ion Activity in Solution," Science, 154, 1553 (1966).

27. E. W. Baumann, "Trace Fluoride Determination with Specific Ion Electrode," Anal. Chim. Acta, 42, 127 (1968).

28. J. L. Stuart, "A Simple Diffusion Method for the Determination of Fluoride," Analyst, 95, 1032 (1970).

29. R. A. Durst, "Fluoride Microanalysis by Linear Null-Point Potentiometry," Anal Chem, 40, 931 (1968).

30. M. S. Frant and J. W. Ross, Jr., "Use of a Total Ionic Strength Adjustment Buffer for Electrode Determination of Fluoride in Water Supplies," Anal Chem, 40, 1169 (1968).

31. C. R. Edmond, "Direct Determination of Fluoride in Phosphate Rock Samples Using the Specific Ion Electrode," Anal Chem, 41, 1327 (1969).

32. J. Tusl, "Direct Determination of Fluoride in Phosphate Materials in Mineral Feeds with the Fluoride Ion Activity Electride," JAOAC, 53, 267 (1970).

33. R. T. Oliver and A. G. Clayton, "Direct Determination of Fluoride in Miscellaneous Fluoride Materials with the Orion Fluoride Electrode," Anal. Chim. Acta, 51, 409 (1970).

34. B. L. Ingram, "Determination of Fluoride in Silicate Rocks Without Separation of Aluminum Using a Specific Ion Electrode," Anal Chem, 42, 1825 (1970).

35. J. C. VanLoon, "The Rapid Determination of Fluoride in Mineral Fluorides Using a Specific Ion Electrode," Anal Lett, 1(6), 393 (1968).

36. W. H. Evans and G. A. Sargent, "The Determination of Small Amounts of Fluorine in Rocks and Minerals," Analyst, 92, 690 (1967).

37. J. L. Guth and R. Wey, "Sur un dosage du fluorure dans les mineral," Crystallogr., 92, 105 (1969).

38. E. J. Duff and J. L. Stuart, "Determination of Fluoride in Calcium Phosphates with a Fluoride-Selective Electrode," Anal. Chim. Acta, 52, 155 (1970).

39. L. Evans, R. D. Hoyle and J. B. McHaskill, "An Accurate and Rapid Method of Analysis for Fluorine in Phosphate Rocks," N. Z. Jl. Sci., 13, 143 (1970); See also H. N. S. Schaefer, Anal Chem, 35, 53 (1963).

40. R. L. Clements, G. A. Sergeant and P. J. Webb, The Determination of Fluorine in Rocks and Minerals by a Pyrohydrolytic Method," Analyst, 96, 51 (1971).

41. H. H. Willard and O. B. Winter, "Volumetric Method for Determination of Fluorine," Ind. Eng. Chem. (Anal. Ed.), 5, 7 (1933).

42. H. H. Willard and C. A. Horton, "Indicators for Titration of Fluoride with Thorium," Anal. Chem. 22, 1190 (1950).

43. D. S. Reynolds, "Further Studies on the Willard and Winter Method for the Determination of Fluorine," J. Assoc. Official Agr. Chemists, 18, 108 (1935).

44. P. J. Kie, L. W. Rieger and H. E. Power, "Determination of Fluoride in Biological Samples by a Nonfusion Distillation and Ion-Selective Membrane Electrode Method," Anal. Chem., 41, 1081 (1969).

45. E. Bellack, "Simplified Fluoride Distillation Method," Am. Water Works Assoc. J., 50, 530 (1958).

46. D. R. Taves, Talanta, 15, 1015-1023 (1968).

47. B. Marshall and R. Wood, Analyst, 94, 493-499 (1969).

48. E. J. Conway, "Microdiffusion Analysis and Volumetric Error," MacMillan Pub. (1958).

49. D. R. Taves, "Separation of Fluoride by Rapid Diffusion Using Hexamethyldisiloxane," Talanta, 15, 969 (1968).

50. J. Tusl, "A Study of the Influence of Silicone Grease on Spectrophotometric Methods of the Determination of Fluoride," Anal. Chem., 41, 352 (1969).

51. W. Funasaki, et al, "Removal of Fluoride Ion with Anion-Exchange Resins," Mem. Fac. Eng., Kyoto Univ., 18, 44-50 (1956).

52. I. Ziphin, W. D. Armstrong and L. Singie, "Chromatographic Separation of Fluoride and Phosphate," Anal. Chem., 29, 310 (1950).

53. H. M. Nielsen, "Determination of Microgram Quantities of Fluoride," Anal. Chem., 30, 1009 (1958).

54. Anon., Health Lab. Sci., 6(2), (1969).

APPENDIX A - TENTATIVE REFERENCE METHOD FOR SAMPLING AND ANALYZING PARTICULATE AND GASEOUS FLUORIDES FROM STATIONARY SOURCES*

1. PRINCIPLE AND APPLICABILITY

1.1 Sampling

1.1.1 Principle - Samples are collected isokinetically by apparatus which provides for the separate collection of particulate and gaseous fluorides.

1.1.2 Applicability - The method is directly applicable for analyzing "dry" streams [where "dry" refers to a relative humidity of less than 100% at stack conditions] from various industrial stationary sources, including the various processes within the primary aluminum, iron and steel, and glass and ceramic industries. With only slight modification (described in Section 11), the method can be applied to analyzing "wet" streams [where "wet" refers to water or steam entrainment in the stream] such as occur for unit operations within the phosphate rock processing industry. In the latter case, particulate and gaseous fluorides cannot be separated.

1.2 Analysis

1.2.1 Principle - Fluoride ion in the collected sample is measured with the fluoride specific ion electrode. If the sample to be analyzed contains particulate, a caustic fusion must be performed to ensure that all fluoride will be soluble. A distillation of the sample from sulfuric acid prior to the electrode measurement is required for removal of interfering ions.

1.2.2 Applicability - The method as written is applicable to any type of sample collected from process effluents which are discharged into the air from unit processes within the primary aluminum, iron and steel, glass and ceramic, and phosphate rock industries. The nature of the sample collected has little effect on the success of the analysis, so that the procedure should be generally applicable to stationary source fluoride emissions from other industries.

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*This method is based on laboratory evaluations, discussions with industrial representatives and reference to the open literature. The method cannot be accepted as final until suitable field tests have been conducted and modifications to the method are made, as appropriate.

2. RANGE AND SENSITIVITY

2.1 Sampling - Not Available

2.2 Analysis - The fluoride electrode can measure fluoride concentrations in the range of 0.02-2,000 μg/ml; however, measurements of less than 0.1 μg/ml require a great deal of care and should be avoided. Since the collected distillate is diluted to 500 ml and a 25-ml aliquot of that solution is then diluted to 50 ml for measurement, the practical lower limit is 100 μg of fluoride; the reagent blank for fusion and distillation averages 10 μg fluoride. The upper limit of fluoride which can be measured successfully.

3. INTERFERENCES

3.1 Sampling - Preliminary measurements indicate that as much as 10% of the total fluoride may be lost in the sampling train, principally through interaction with the probe. Also, physical and chemical adsorption of gaseous fluorides onto particulate can effect the apparent gaseous to solid fluoride distribution.

3.2 Analysis - Metals such as aluminum, iron and lead form soluble fluoride complexes reducing the fluoride vapor pressure which can result in incomplete evolution of fluoride during distillation. Silica forms a precipitate which entraps fluoride, sticks to the walls of the still pot and prevents complete evolution of fluoride.

Maximum amounts of these interferences which can be tolerated have not been determined as a function of fluoride concentration. However, initial results indicate that for 10 μ moles of fluoride, the presence of more than 1 mmole of silicon or iron, more than 5 mmoles of lead, or more than 10 mmoles of aluminum can adversely affect distillation recovery.

4. PRECISION, ACCURACY AND STABILITY

4.1 Sampling

4.1.1 Precision - Not Available

4.1.2 Accuracy - Not Available

4.1.3 Stability - The particulate catch, probe washings, and impinger solutions remain stable and unchanged for at least a month as long as they are stored in sealed polyethylene or flint glass containers.

4.2 Analysis - Reliable estimates of precision, accuracy and stability when analyzing field samples are not yet available. Although very tentative, some estimates drawn from laboratory studies are present below.

4.2.1 Precision - At the 2 mg fluoride level, a relative standard deviation of ± 2% or better was achieved on sets of quadruplicate samples.

4.2.2 Accuracy - Accuracy depends first upon the accuracy with which the fluoride content of the standardization samples is known. The more important limitation on accuracy is the effect of metals (see 3.2) on distillation recovery. Within the constraints of 3.2, 95% or better recovery can be achieved.

4.2.3 Stability - The one source of instability in the method is potential drift in the electrode response. A calibration curve, if used, should be generated daily and a known, mid-range standard should be measured as a check at least once per hour. If direct readout is employed, the span should be checked hourly.

Electrode response is temperature sensitive; concentration indicated will change by about 1.5%/°C. If ambient lab temperature fluctuates more than a few degrees, it is advisable to plan samples in a water bath prior to measurement. If an electrically-driven magnetic stirrer is used, precaution should be taken to see that it does not heat the solution.

5. APPARATUS

5.1 Sampling

5.1.1 Sample Probe - A 5-foot (or longer) by 1/2 to 5/8 inch diameter 316 stainless steel with stainless steel nozzle and orifice;

or

A 5-foot by 1/2 to 5/8 inch diameter borosilicate glass tubing encased in a metal support tube fitted with a stainless steel nozzle and orifice, both with provision for heating the probe to maintain a gas temperature of 250°F.

5.1.2 Particulate Collector - A 316 stainless steel or Pyrex filter holder with suitable filter media (glass fiber, organic membrane, or paper);

or

A stainless steel enclosed electrostatic precipitator as described in Reference A-1; both systems including a heating system capable of maintaining any temperature up to 250°F.

5-1.3 Impingers - Two, 500 ml Greenburg-Smith impingers, made from polyethylene or glass and containing 200 ml of distilled water, to be contained in an ice bath.

5.1.4 Mist Trap - A 500 ml bottle containing 175g of dried silica gel for protection of down stream components from moisture.

5.1.5 Vacuum Pump - Rated at 4 cfm at 0 in.Hg and 9 cfm at 26 in.Hg.

5.1.6 Dry Gas Meter - Rated at a maximum of 175 cu. ft. per hour.

5.1.7 Air Flowmeter - A calibrated rotameter or critical orifice capable of measuring airflow within 2% over the range of 1 to 50 ft/sec.

5.2. Analysis

5.2.1 Fusion Crucible - Crucible, nickel or Inconel, 60 ml capacity.

5.2.2 Distillation Assembly - Glassware (shown in Figure A-1) consisting of a 1-liter, round bottom, borosilicate boiling flask(b), and adapter with a thermometer opening(c), a 300 mm Graham condenser(f), and a thermometer reading to 250°C(d). Standard taper or spherical ground-glass joints shall be used throughout.

Heat is provided by a hemispherical heating mantle(a) connected to a laboratory variable transformer. Distillate is collected in a 500-ml volumetric flask(g).

5.2.3 Fluoride Specific Ion Electrode System

5.2.3.1 Fluoride Ion Specific Electrode (Orion Model 94-09 or equivalent solid-state fluoride ion activity sensing electrode using a rare-earth doped lanthanum fluoride crystal)

5.2.3.2 Reference Electrode - Silver/silver chloride or saturated Calomel suitable for use with the fluoride electrode and electrometer used. A large area liquid junction is preferable to a fiber-type liquid junction.

5.2.3.3 Electrometer (more commonly a pH meter with millivolt scale, or a "Specific Ion Meter" made specifically for ion-specific electrode use) capable of ± 0.5 mv. resolution.

6. REAGENTS

6.1 Sampling

6.1.1 Distilled Water

6.2 Analysis

6.2.1 Fusion Flux - Either NaOH or Na_2CO_3/K_2CO_3 (equimolar mixture) may be used. Flux components shall be ACS reagent grade.

6.2.2 Calcium Oxide - Fluoride content less than 50 ppm.

6.2.3 Concentrated Sulfuric Acid - ACS Reagent grade.

6.2.4 Citrate Buffer - 1.0 M stock solution. Dissolve 294.1 g of reagent grade $Na_3C_6H_5O_7 \cdot 2H_2O$ (Fisher CERTIFIED, or equivalent) in 1 liter of distilled water.

6.2.5 Bromthymol Blue Indicator Solution - A 0.4% aqueous solution is commercially available.

6.2.6 Fluoride Standard Solution - A 0.1M fluoride standard solution is commercially available, or it can be prepared by dissolving ACS Reagent grade sodium fluoride in water.

7. PROCEDURE

7.1 Sampling

7.1.1 Prior to sampling, measure stack gas velocity at a series of test points to determine the velocity profile of the stack, using procedure given in Reference A-2. If variation is 10% or less, sampling may be carried out at point of average velocity. If variation exceeds 10%, sampling must be carried out incrementally at a series of test points to reflect an average velocity per the procedure given in Reference A-2.

7.1.2 Sampling will be isokinetic at a rate between 0.75 and 1.25 cfm.

7.1.3 Sampling time will reflect all cyclic variations in the process being monitored, but will not be less than 60 minutes.

7.1.4 After completion of sampling, the train shall be disassembled and the collected materials placed in polyethylene storage containers. The final volume of the impinger catch together with the weight increase of the silica gel will be noted to calculate moisture content of the gas. Separate containers will be used for the particulate catch, impinger catch and washings, and probe washings.

7.2 Analysis

7.2.1 Preparation of Sample for Distillation - Whether the fluoride samples have been collected by an electrostatic precipitator in NaOH solutions, or on filters, they generally require some treatment before a distillation can be made. Organic matter must be destroyed without incurring any fluoride losses, and large volumes of solution may need to be evaporated to volumes which will permit their placement in the distilling flasks. Several precautions are mandatory when preparing samples for distillation.

7.2.1.1 Filter Paper Sample - Fold the filter paper with the clean side out and place in a nickel or Inconel crucible. Saturate the paper with saturated lime water solution prepared from fluoride-free CaO. Complete saturation of the paper is essential to prevent loss of fluoride. Heat the crucible and contents on a hot plate to remove excess water. When dry, ash the sample in a muffle furnace at a temperature not in excess of 600°C until no carbon remains. Ordinarily this is accomplished in less than 1 h. Remove the crucible from the furnace, cool, and add 3 g of NaOH (or 4.5 g mixed carbonates). Fuse the contents over a burner for ten minutes, and then allow to cool to a temperature less than 100°C.

7.2.1.2 Glass Fiber Filter Sample - Proceed in accordance with 7.2.1.1 for filter papers except to omit the ashing step.

7.2.1.3 Organic Membrane Filter Sample - Proceed in accordance with 7.2.1.1 for filter papers, except to omit folding, and thoroughly char the filter on the hot plate at low heat, prior to ignition. Excessive heat causes an instantaneous ignition of the filter with an attendant loss of sample.

7.2.1.4 Impinger Sample - Depending on whether or not a filter or electrostatic precipitator was used ahead of the impingers in the sampling train, the impinger sample can be either a clear solution or can contain suspended or settled solids.

If the impinger sample contains no undissolved solids, it is ready for distillation. If the sample volume is greater than 300 ml, a 300 ml aliquot can be taken for distillation; if the fluoride level is low, the volume can be reduced to 300 ml or less by first adding 0.1 g CaO and then evaporating on a steam bath. During evaporation, care must be taken to avoid mechanical losses due to splattering.

If the impinger sample contains insoluble particulate, it should be filtered and the filtrate set aside while the filter paper and collected solids are treated as in 7.2.1.1. (If the impinger sample containing insoluble particulate is greater than 300 ml in volume, 0.1 g of CaO should be added and the solution volume reduced by evaporating over a steam bath prior to performing the filtration.) After the solids which were filtered out of the impinger sample have been ashed and fused, and the fusion allowed to cool, the fusion solids along with the impinger sample filtrate are ready to be transferred together into the distillation flasks.

7.2.1.5 Electrostatic Precipitator Sample - Wash the contents of the precipitator into a 250 ml nickel or Inconel beaker with distilled water. Add 0.1 g CaO and 3 g of NaOH, evaporate to dryness, and fuse over a burner for 10 minutes. Allow the fusion to cool to less than 100°C.

7.2.2 Distillation

7.2.2.1 Charging the Flask with Acid and Adjusting the Acid/Water Ratio - Before the actual samples can be distilled, the distilling flask must be charged with a mixture of sulfuric acid and water and the acid/water ratio adjusted by distilling the contents of the flask until the pot temperature reaches exactly 210°C. This pre-distillation also serves to strip out traces of fluoride in the H_2SO_4. Place 400 ml of water in the distilling flask and add 200 ml of concentrated H_2SO_4. Observe the usual precautions while mixing the H_2SO_4; the acid should be added slowly with constant swirling of the flask. Add about a half dozen glass beads and assemble the apparatus as shown in Figure A-1. The electric heating mantle is then turned on and the distillation of the initial acid/water charge is allowed to proceed until the temperature of the still pot reaches exactly 210°C. The heat is then immediately removed and the temperature of the still pot allowed to cool to less than 60°C before proceeding to add the first fluoride sample. The distillate that was collected during this initial adjustment of the acid/water ratio is of no use and is discarded.

7.2.2.2 Distillation - The sample in a total liquid volume of 300 ml is then slowly transferred into the distilling flask with good mixing by swirling. Solid samples from fusions should be broken up with a spatula, the fine chunks introduced directly into the flask with the aid of a water wash, and additional water added so that the total volume added to the distilling flask is about 300 ml. In this case, the exact volume is not critical. However, in the case of fluoride-containing solutions with a volume greater than 300 ml, if an aliquot is taken for introduction into the still, the volume of the aliquot must obviously be known accurately.

7.2.3 Analysis

7.2.3.1 Calibration - Fluoride standards are prepared by taking aliquots of the 0.1 M stock solution, adding 5.0 ml of 1 M citrate buffer, and diluting to a final volume of 50 ml. For wide dynamic range measurements, seven standards spanning the range $10^{-2} - 10^{-6}$ M are adequate. The standards are measured and a calibration curve (millivolts vs. log concentration) is constructed.

For measurements over a narrower range, certain meters may be calibrated to read directly in ppm fluoride by calibration with two known solutions.

7.2.3.2 Measurement - The collected distillate ($\leq$210°C) is diluted to 500 ml and a 25 ml aliquot is pipetted into a 50 ml volumetric flask. Four drops of bromthymol blue are added and, if necessary, pH adjusted to be in the range of 6.6 - 7.1 (indicator is green in color). Five milliliters of 1.0 M citrate buffer is added, and the resulting solution diluted to 50 ml.

The solution is transferred into a beaker, the fluoride electrode immersed and the EMF in millivolts (or ppm F if instrument is direct reading) is read. Concentration of fluoride is read from the calibration curve.

8. CALIBRATION, STANDARDS, AND EFFICIENCIES

8.1 Sampling - Not available.

8.2 Analysis - The electrode measurement is calibrated daily and checked hourly. Fusion and distillation are not normally calibrated but assumed to be quantitative. Tests to date indicate that this assumption is valid, but field testing is required to substantiate it. The entire method should be run occasionally at appropriate times using a primary standard such as ACS Reagent grade NaF or a collaboratively analyzed standard sample of a material such as cryolite or phosphate rock to ensure that it is indeed working properly in a particular laboratory for a particular analyst.

9. CALCULATIONS

9.1 Sampling - From measurements of gas temperature, barometric pressure and collected volume of water, calculate dry gas volume and total gas volume at standard conditions. These volumes are required for subsequent calculations of fluoride concentration.

9.2 Analysis - Total mg F in the submitted sample is computed from the mg/ml value derived from the calibration curve as follows:

$$\text{milligrams F} = (\text{mg/ml}) \times 1000 \times \frac{\text{total sample volume received}}{\text{volume of sample aliquot taken}}$$

10. REFERENCES

10.1 Sampling

A-1 G. L. Rounds and H. J. Matoi. "Electrostatic Sampler for Dust-Laden Gases," Anal. Chem. 27, 1955, 829-830.

A-2 "Standards of Performance for New Stationary Sources," Federal Register 36, August 17, 1971, 15704-15722.

10-2 Analysis

A-3 ASTM Method D1606-60 "Standard Method of Test for Inorganic Fluoride in the Atmosphere."

A-4 ASTM Method D1179-68 "Standard Method of Test for Fluoride Ion in Industrial Water and Industrial Waste Water."

11. MODIFICATION FOR MEASUREMENT OF WET GAS STREAMS

The procedure for measuring fluorides in wet gas stream is the same as above, except for the following modifications:

5.1.2 Delete

7.1.4 Change third sentence to: The impinger catch and washings and the probe washings will be combined and placed in one container.

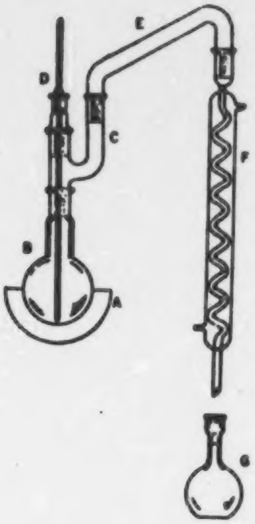

Figure A-1 Distillation Assembly for Fluoride Insolation

A. Electric Heat Mantle
B. Round-bottom flask, 1000 ml
C. Adapter with thermometer opening
D. Thermometer 250°C
E. Connecting tube
F. Graham condenser, 300 mm
G. Volumetric flask, 500 ml

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